PROTHIOCONAZOLE (232)

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EXPLANATION

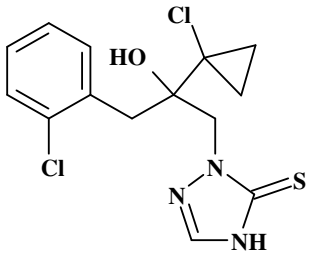
Prothioconazole is a systemic fungicide with a triazolinthione structure. At the 39th session of the CCPR (ALINORM 07/30/24), it was listed as a candidate for evaluation of new compounds by the 2008 JMPR.

The manufacturer submitted information on physical and chemical properties, metabolism, analytical method, environmental fate, supervised trials processing and national registered uses.

IDENTITY

Common name:	Prothioconazole
Manufacturer's code Number:	JAU 6476
Other code numbers:	CAS number: 178928-70-6
	CIPAC number:745
Chemical name:	IUPAC:2-[(2RS)-2-(1-chlorocyclopropyl)-3-(2-chlorophenyl)-2-hydroxypropyl]-2H-1,2,4-triazole-3(4H)-thione
	CAS:2-[2-(1-chlorocyclopropyl)-3-(2-chlorophenyl)-2-hydroxypropyl]-1,2-dihydro-3H-1,2,4-triazole-3-thione
Formulae:	$C_{14}H_{15}Cl_2N_3OS$
Molecular mass	344.26

Structural formula:



Racemate (50:50)

PHYSICAL AND CHEMICAL PROPERTIES

The manufacturing process is not enatio-selective. All technical quality JAU 6476 is produced as a 50:50 racemate.

Description of test materials used

Prothioconazole, pure, LOT M00729, purity 99.4%

[phenyl-UL-^{14}C] prothioconazole, radiochemical purity > 99%, specific radioactivity 2.97 MBq/mg (batch KML 2468, lot 11403/1)

[phenyl-UL-^{14}C]-prothioconazole, radiochemical purity > 99%, specific radioactivity 3.66 MBq/mg (batch KML 2720, lot 12268/3)

[phenyl-UL-^{14}C]-prothioconazole, radiochemical purity > 99%, specific radioactivity 1.85 MBq/mg (batch KML 2761, lot 13094/1)

[3,5-Triazole-^{14}C] prothioconazole, radiochemical purity > 99%, specific radioactivity 1.94 MBq/mg (batch THS 5018, lot 10708/17)

Prothioconazole, pure, LOT M00175, purity 99.9%

Prothioconazole, technical., batch 06233/0040, purity 98.3%

Property	Material, Method	Results	Reference
Physical state, colour, odour	Material 1 visual	Pure active ingredient: Colour: colourless to faintly beige powder with faint, uncharacteristic odour Active substance as manufactured; colourless to faintly beige powder	Schneider, 2001
Melting point	Material 1 OECD 102 EC A.1.	Melting range: 139.1 °C–144.5 °C	Schneider, 2001
Boiling point	Material 1	487 °C ± 50 °C (calculated)	Schneider, 2001
Temperature of decomposition or sublimation	Material 1 OECD 113	Prothioconazole was found thermally stable at ambient temperature under air. No exothermic reaction was observed until 230 °C	Eberz, 2001
Relative density	Material 1 OECD 109 EC A.3.	1.36 g/mL at 20 °C	Schneider, 2001
Vapour pressure	Material 1 OECD 104 EC A.4.	<< 4×10^{-7} Pa at 20 °C << 4×10^{-7} Pa at 25 °C	Schneider, 2001
Henry's law constant	calculated	<< 3×10^{-5} Pa × m^3 /mole at 20 °C	Schneider, 2001
Solubility in water including effect of pH	Material 1 OECD 105, EC A.6. flask method	0.005 g/L at 20 °C at pH 4 0.3 g/L at 20 °C at pH 8 2.0 g/L at 20 °C at pH 9	Schneider, 2001
Solubility in organic solvents	Material 1 flask method[1]	n-heptane < 0.1 g/L at 20 °C xylene 8 g/L at 20 °C 1-octanol 58 g/L at 20 °C 2-propanol 87 g/L at 20 °C ethyl acetate > 250 g/L at 20 °C polyethylene glycol > 250 g/L at 20 °C acetonitrile 69 g/L at 20 °C acetone > 250 g/L at 20 °C dimethylsulfoxide 126 g/L at 20 °C dichloromethane 88 g/L at 20 °C	Schneider, 2001
Partition coefficient in n-octanol/water at 20 °C	Material 1 OECD 107	unbuffered: Pow 11300, log Kow 4.05 pH 4: Pow 14600, log Kow 4.16 pH 7: Pow 6600, log Kow 3.82 pH 9: Pow 100, log Kow 2.00	Schneider, 2001

Property	Material, Method	Results	Reference
Hydrolysis rate	Material 2 EEC method C.7, SETAC, EPA 161-1	The hydrolysis under sterile conditions in the dark at 50 °C at pH 4, 7 and 9. DT_{50} at 50 °C: pH 7 and 9: > 1 year, pH 4: 120 days DT_{50} at 25 °C (extrapolated): more than one year at any pH under environmental conditions.	Riegner, 1998
Photochemical degradation	Material 3, 4, 5, 6 SETAC, EPA 161-2	Experimental half-lives at pH 7 and 25 °C were determined to be 47.7 hours (mean of two labels). Under the experimental conditions prothioconazole was completely photodegraded.	Gilges and Bornatsch, 2001
		Estimated direct photolysis half-lives ranged from 50 to > 200 days at pH 4, and 7 to 20 days at pH 9 for the periods of main use.	Hellpointner, 2001
Dissociation constant	Material 1	pKa = 6.9 dissociation product: see appendix below	Schneider, 2001 Linke-Ritzer, 2004

The solubility of prothioconazole in organic solvents was determined by liquid chromatography. This method is specific for the active ingredient. That means that the results are not affected by minor differences in the purity of the test substance as they may occur in the technical active substance. Therefore it is expected that the solubility data for the pure active substance reflect the solubility of the technical active substance.

Photolysis of prothioconazole (Gilges and Bornatsch, 200)

The photodegradation of prothioconazole was studied in sterile aqueous buffer solution at pH 7 and 5 °C using [phenyl-UL-14C] and [3,5-Triazole-14C]prothioconazole. Under the experimental conditions prothioconazole was completely photodegraded. Experimental half-lives were determined to be 47.7 hours (mean of two labels).

Prothioconazole-desthio *(M04)* was identified as the main degradation product at a maximum level of 56% of the applied radioactivity. Two further major metabolites were identified as prothioconazole-thiazocine *(M12)* at 15% and 1,2,4-triazole *(M13)* at 12%.

Recovery at the latest sampling intervals ranged from 103.9% to 107.2% of the applied radioactivity.

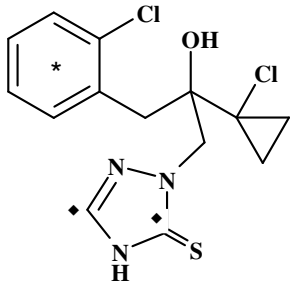
Formulations

Prothioconazole is formulated for seed treatment and foliar applications.

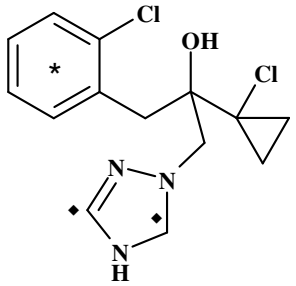
Formulation	Content of active substance	Trade name (country/region related)
Seed treatment products (e.g.)		
FS 100	100 g/L Prothioconazole	Redigo
FS 400	250 g/L Prothioconazole	Lamardor
FS 075	37.5 g/L Prothioconazole	Bariton
FS 076.25	25 g/L Prothioconazole	Efa
Spray formulation products (e.g.):		
EC 250	250 g/L Prothioconazole	Proline, Input Pro, Joao
SC 480	480 g/L Prothioconazole	Rudis , Proline
EC 250	125 g/L Prothioconazole	Prosaro
EC 200	100 g/L Prothioconazole	Fandango
EC 460	160 g/L Prothioconazole	Input, Helix

METABOLISM AND ENVIRONMENTAL FATE

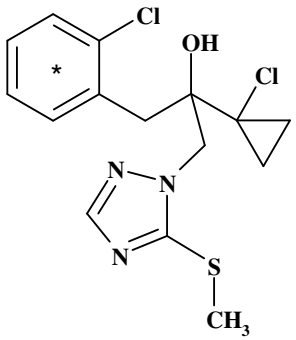
The metabolism of prothioconazole in plants and animals was investigated using [phenyl-UL-^{14}C]-prothioconazole referred to as phenyl-label, and [3,5-triazole-^{14}C]-labelled parent compound referred to as triazole-label.



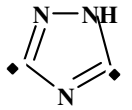
In addition, studies were conducted using [phenyl-UL-^{14}C]- and [3,5-triazole-^{14}C]-labelled prothioconazole-desthio *(M04)*.



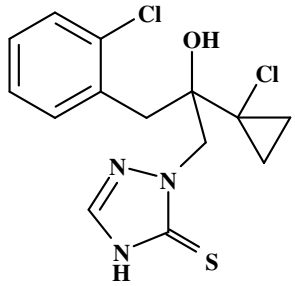
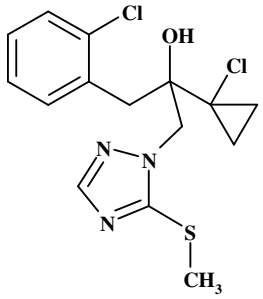
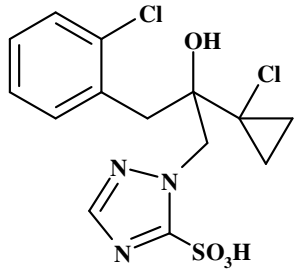
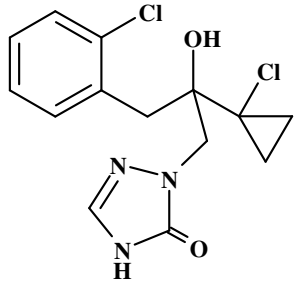
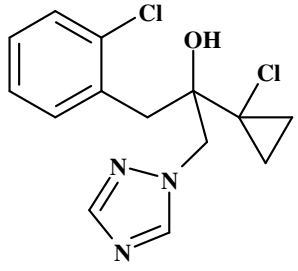
Studies on the fate and behaviour of prothioconazole in the environment were performed using [phenyl-UL-^{14}C]- and [3,5-triazole-^{14}C]-labelled as well as the non-labelled parent compound. In addition, studies with the metabolites prothioconazole-S-methyl *(M01)* and prothioconazole-desthio *(M04)* were investigated using [phenyl-UL-^{14}C]-labelled compounds.

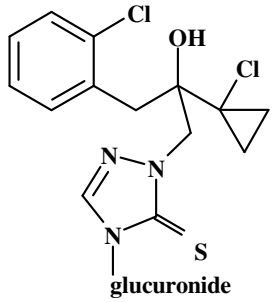
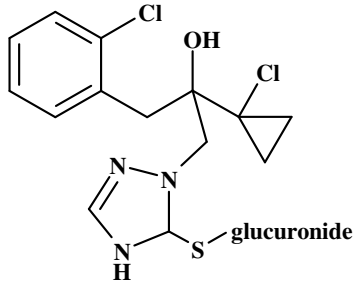
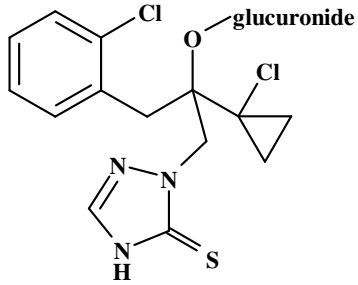
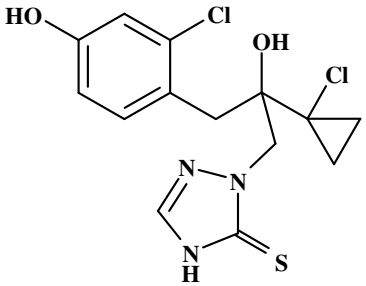
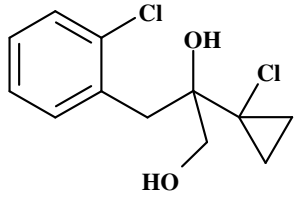


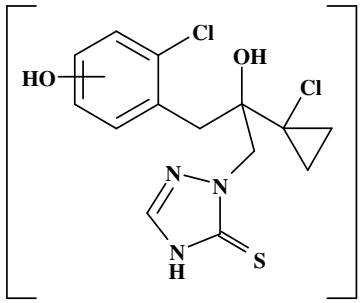
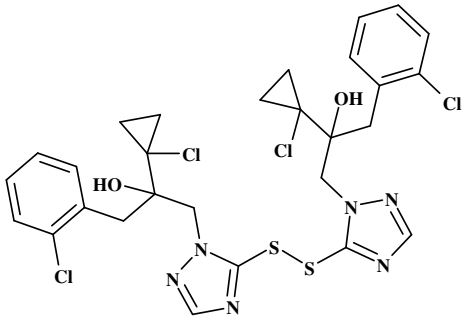
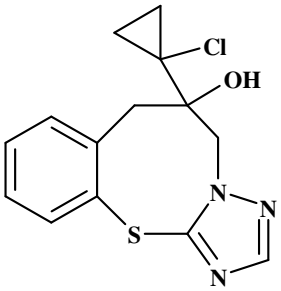
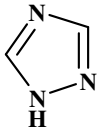
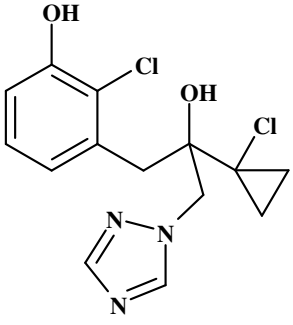
[3,5-Triazole-^{14}C]-labelled 1,2,4-triazole *(M13)* was used in a supplementary freezer storage stability study.

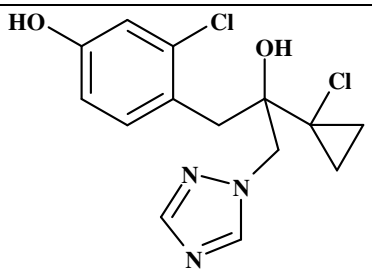
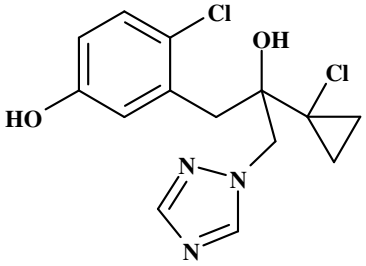
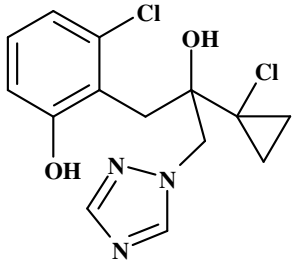
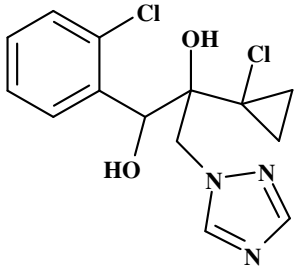
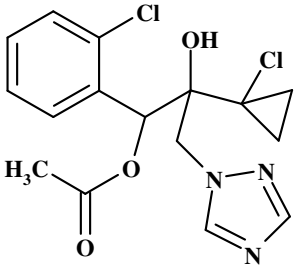
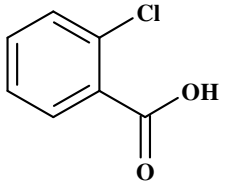


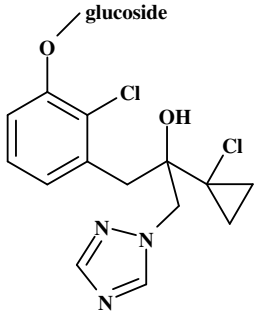
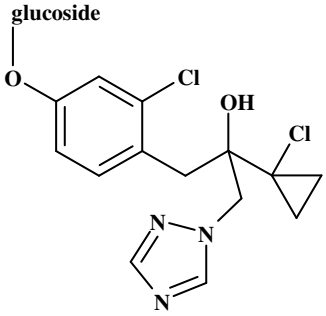
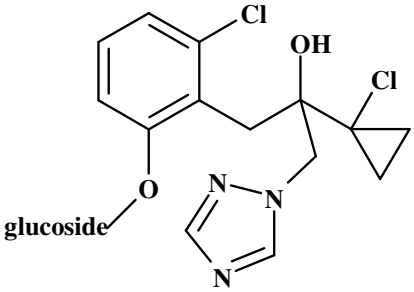
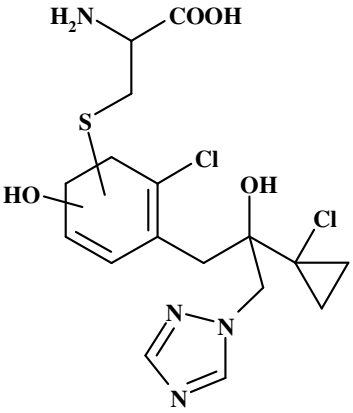
The following table shows the structures, codes and names of prothioconazole and all related metabolites referred to within this document. These designations are sometimes different for those used by the study authors.

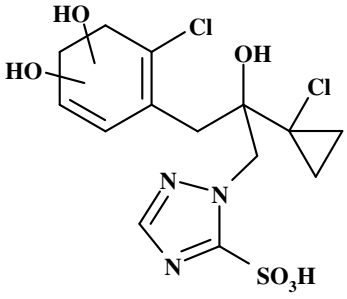
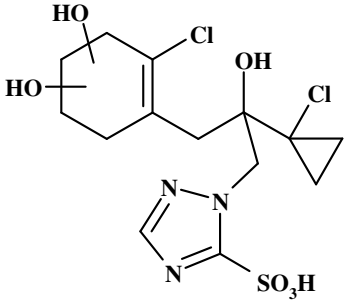
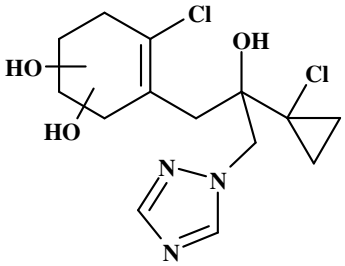
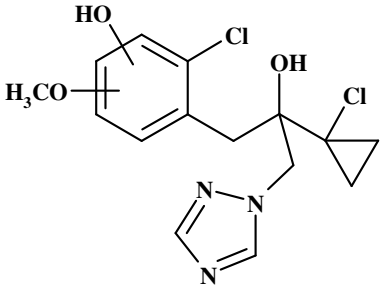
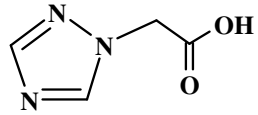
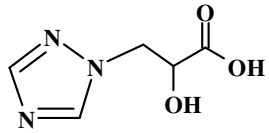
No.:	Structural formula	Name used in the summary CA index name [CAS#] if available Identified in metabolism or other studies
ai		Prothioconazole (JAU 6476) CAS: 178928-70-6 animal: rat, goat, hen plant: peanut, sugar beet, wheat rotational crop soil: aerobic, photolysis, field dissipation, column leaching, water: hydrolysis, photolysis, aerobic & anaerobic
M01		JAU 6476-S-methyl CAS: 178928-71-7 animal: rat, goat, hen soil: aerobic, column leaching, water: aerobic & anaerobic
M02		JAU 6476-sulfonic acid animal: plant: peanut, sugar beet, wheat rotational crop soil: aerobic, photolysis, aged column leaching
M03		JAU 6476-triazolinone animal: rat plant: peanut, sugar beet, wheat rotational crop soil: aerobic, photolysis water: aerobic
M04		JAU 6476-desthio CAS: 120983-64-4 animal: rat, goat, hen plant: peanut, sugar beet, wheat rotational crop soil: aerobic, photolysis, field dissipation, column leaching, water: hydrolysis, photolysis, aerobic

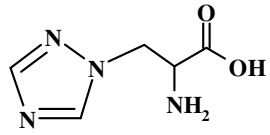
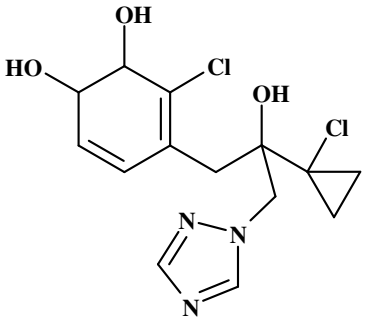
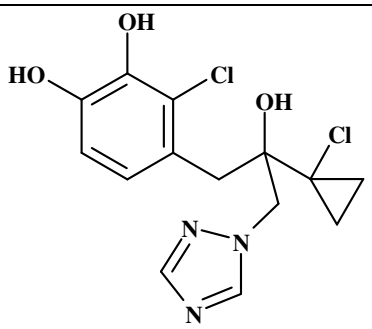
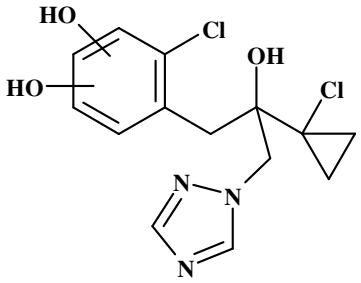
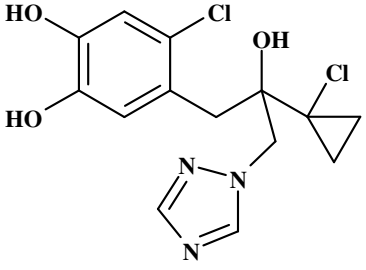
No.:	Structural formula	Name used in the summary CA index name [CAS#] if available Identified in metabolism or other studies
M05		JAU 6476-N-glucuronide animal: rat, goat, hen
M06		JAU 6476-S-glucuronide animal: rat, goat, hen
M07		JAU 6476-O-glucuronide
M08		JAU 6476-4-hydroxy animal: rat, goat, hen
M09		JAU 6476-benzylpropyldiol plant: peanut [a], wheat [b] rotational crop [a] after hydrolysis only [b] probably M09 was taken up by the roots and translocated as M03 into the shots

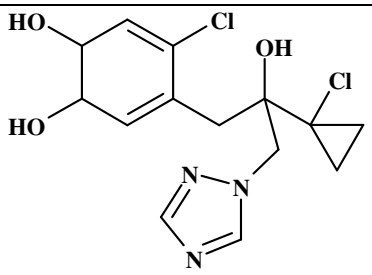
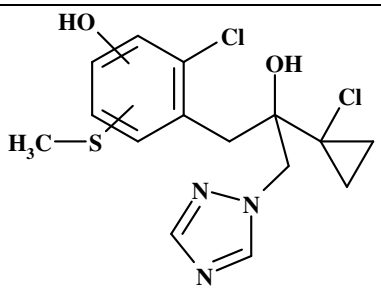
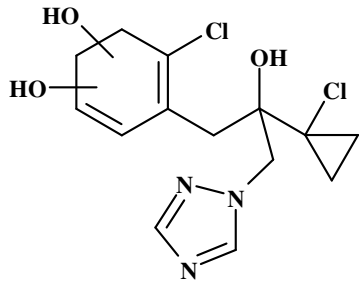
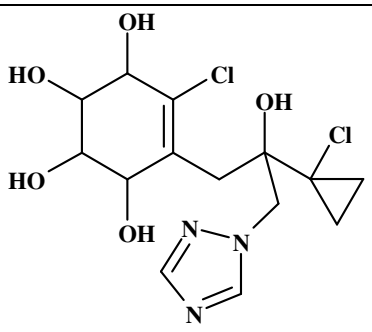
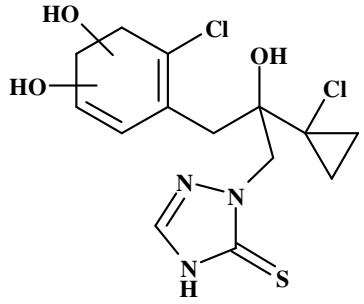
No.:	Structural formula	Name used in the summary CA index name [CAS#] if available Identified in metabolism or other studies
M10	 **glucuronide**	JAU 6476-hydroxy-glucuronide animal: goat, hen
M11		JAU 6476-disulfide plant: peanut, wheat rotational crop
M12		JAU 6476-thiazocine water: photolysis
M13		1,2,4-triazole CAS: 288-88-0 animal: rat, hen soil: aerobic[a] water: photolysis, aerobic [a] below LOQ
M14		JAU 6476-desthio-3-hydroxy animal: rat, goat, hen plant: peanut, sugar beet[a], wheat rotational. crop soil: aerobic[b] [a] M14/M15/M16/M17 [b] M14/M15/M16

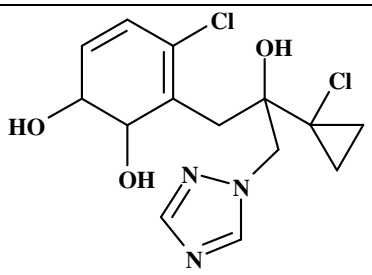
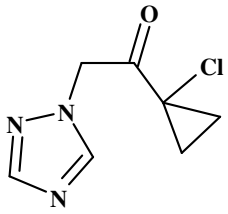
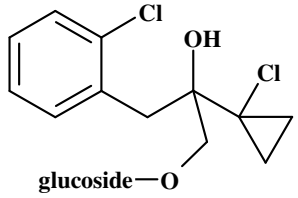
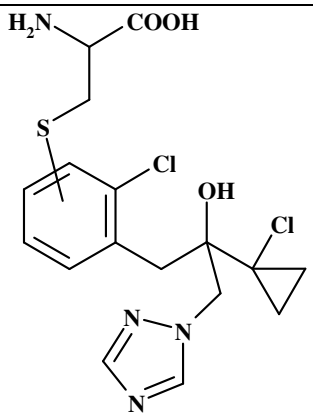
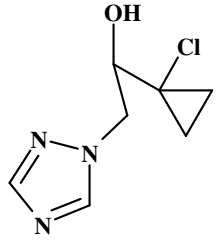
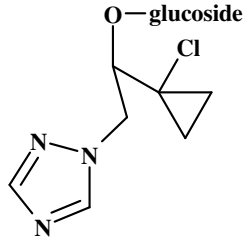
No.:	Structural formula	Name used in the summary CA index name [CAS#] if available Identified in metabolism or other studies
M15		JAU 6476-desthio-4-hydroxy animal: rat, goat, hen plant: peanut, sugar beet[a], wheat rotational crop soil: aerobic [b] [a] M14/M15/M16/M17 [b] M14/M15/M16
M16		JAU 6476-desthio-5-hydroxy plant: sugar beet[a], wheat[a] soil: aerobic[b] [a] M14/M15/M16/M17 [b] M14/M15/M16
M17		JAU 6476-desthio-6-hydroxy plant: sugar beet[a], wheat rotational. crop soil: aerobic [a]M14/M15/M16/M17
M18		JAU 6476-desthio-α-hydroxy plant: peanut[a], sugar beet , wheat rotational crop [a] after hydrolysis only
M19		JAU 6476-desthio-α-acetoxy plant: wheat rotational. crop *(MR-159/00)*
M20		2-chlorobenzoic acid CAS: 118-91-2 soil: aerobic[a] [a] < LOQ

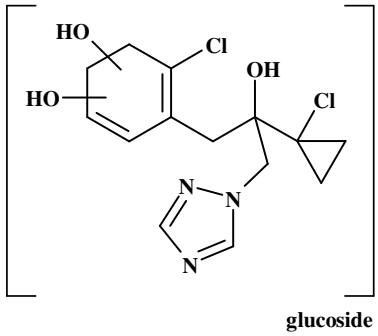
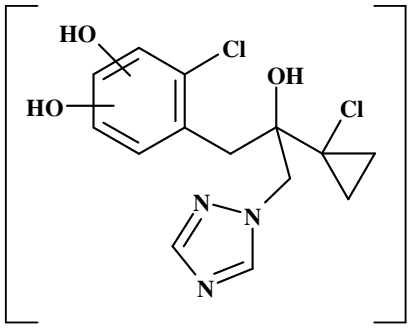
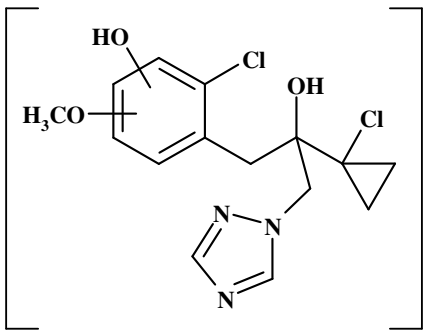
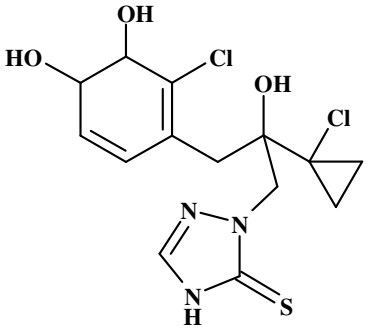
No.:	Structural formula	Name used in the summary CA index name [CAS#] if available Identified in metabolism or other studies
M21		JAU 6476-desthio-3-hydroxy-glucoside glucoside of M14 plant: peanut[a], sugar beet[b], wheat[b] rotational crop[c] [a] M21/M22 [b] M21/M22/M23 [c] tentatively identified as M21 or M22 or M23
M22		JAU6476-desthio-4-hydroxy-glucoside glucoside of M15 plant: peanut[a], sugar beet[b], wheat[b] rotational crop[c)] [a] M21/M22 [b] M21/M22/M23 [c] tentatively identified as M21 or M22 or M23
M23		JAU 6476-desthio-6-hydroxy-glucoside glucoside of M17 plant: sugar beet[a], wheat[a] rotational crop[b] [a] M21/M22/M23 [b] tentatively identified as M21 or M22 or M23
M24		JAU 6476-desthio-hydroxy-dienyl-cysteine plant: peanut , sugar beet

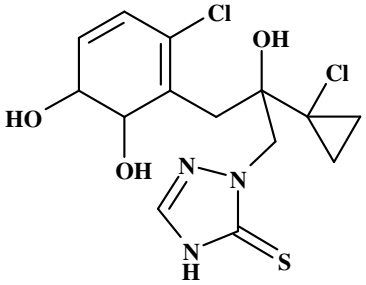
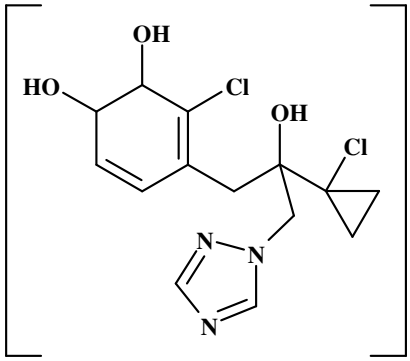
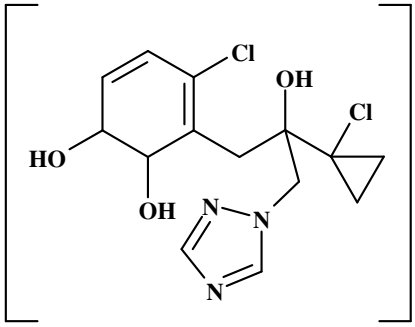
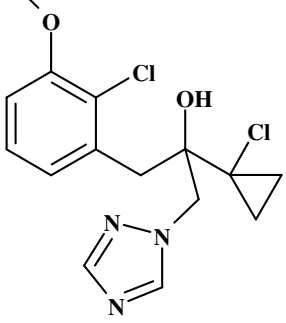
No.:	Structural formula	Name used in the summary CA index name [CAS#] if available Identified in metabolism or other studies
M25		JAU 6476-dihydroxy-diene-sulfonic acid plant: peanut[a] [a] M25/M26
M26		JAU 6476-dihydroxy-olefin-sulfonic acid plant: peanut[a] [a] M25/M26
M27		JAU 6476-desthio-dihydroxy-olefin plant: rotational crop[a] [a] mentioned in the pathway only, M64 tentatively identified
M28		JAU 6476-desthio-hydroxy-methoxy animal: rat, goat[a] [a] mentioned in the pathway
M29		Triazolylacetic acid (TAA) plant: peanut, wheat rotational crop
M30		Triazolylhydroxypropionic acid (THP) plant: peanut , sugar beet, wheat rotational crop

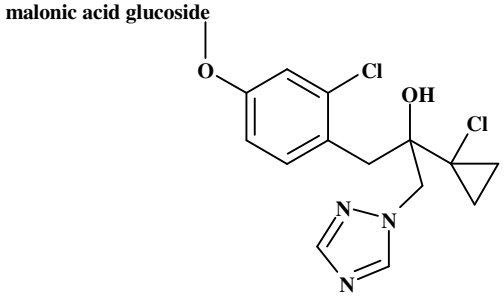
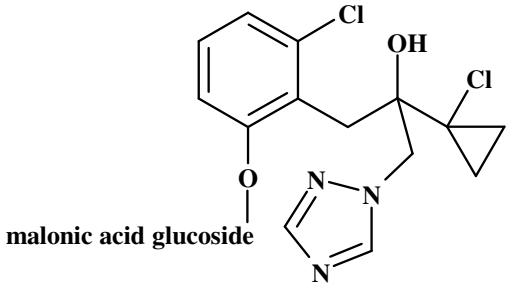
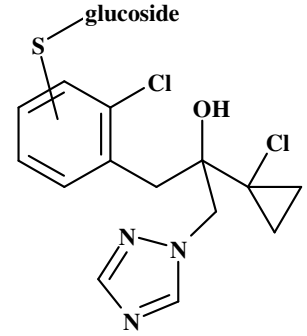
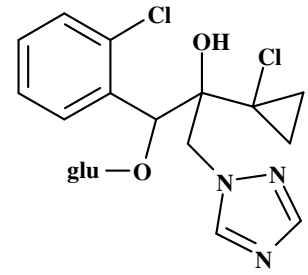
No.:	Structural formula	Name used in the summary CA index name [CAS#] if available Identified in metabolism or other studies
M31		Triazolylalanine (TA) plant: peanut , sugar beet, wheat rot. crop
M32		JAU 6476-desthio-3,4-dihydroxy-diene animal: rat[a], goat [a] M32/M38
M33		JAU 6476-desthio-3,4-dihydroxy animal: goat
M34		JAU 6476-desthio-dihydroxy animal: rat , goat
M35		JAU 6476-desthio-4,5-dihydroxy animal: rat, goat[a] [a] M04 as test substance

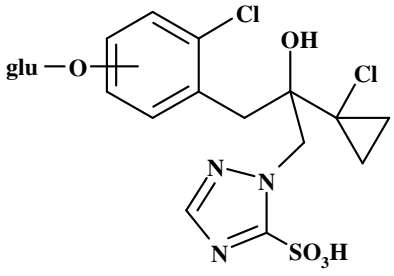
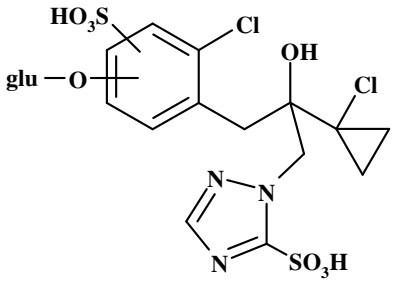
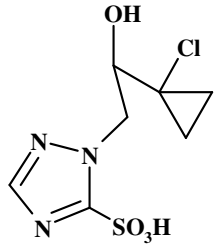
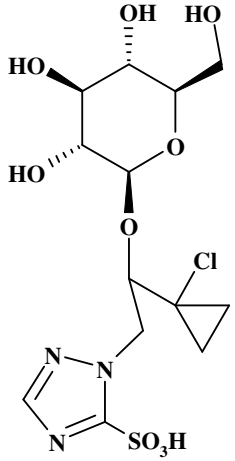
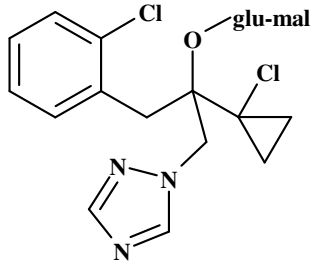
No.:	Structural formula	Name used in the summary CA index name [CAS#] if available Identified in metabolism or other studies
M36		JAU 6476-desthio-4,5-dihydroxy-diene animal: goat[a,b] [a] M04 as test substance [b] mentioned in the pathway
M37		JAU 6476-desthio-hydroxy-S-methyl animal: plant: soil: water:
M38		JAU 6476-desthio-dihydroxy-diene animal: rat[a], goat[b] [a] M32/M38 [b] M38 (M32/M41)
M39		JAU 6476-desthio-olefin-tetrahydroxy animal: rat[a] [a] M04 as test substance
M40		JAU 6476-dihydroxy-diene animal: goat, hen

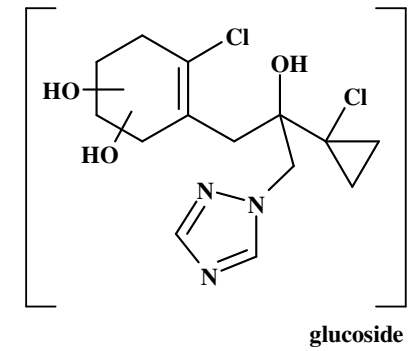
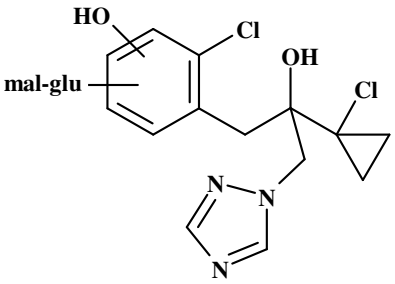
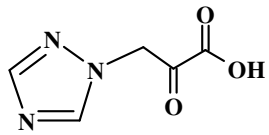
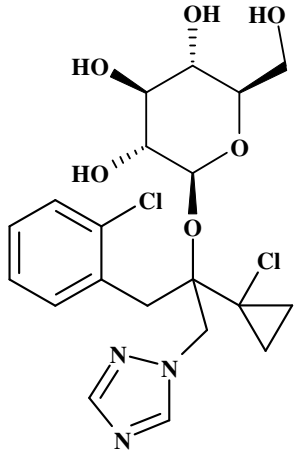
No.:	Structural formula	Name used in the summary CA index name [CAS#] if available Identified in metabolism or other studies
M41		JAU 6476-desthio-5,6-dihydroxy-diene animal: goat[a] [a] M38 (M32/M41)
M42		JAU 6476-triazolylketone water: aerobic metabolism
M43		JAU 6476-benzylpropyldiol-glucoside glucoside of M09 plant: wheat[a] rotational crop [a] probably M09 was taken up by the roots and translocated as M43 into the shoots
M44		JAU 6476-desthio-phenyl-cysteine plant: peanut, wheat
M45		JAU 6476-triazolyl-ethanol plant: peanut, sugar beet, wheat rotational crop
M46		JAU 6476-triazolyl-ethanol-glucoside glucoside of M45 plant: peanut, sugar beet, wheat rotational crop

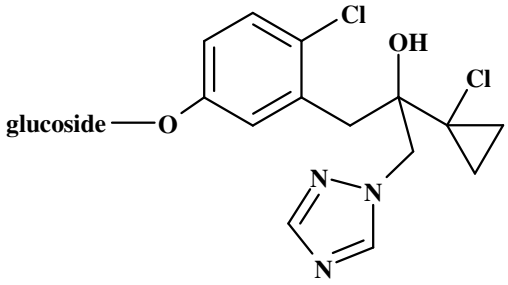
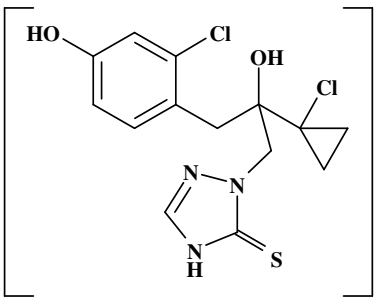
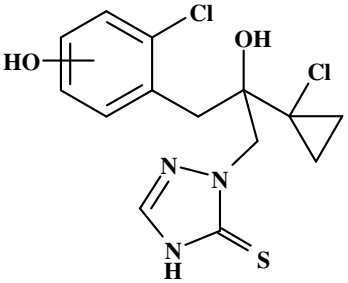
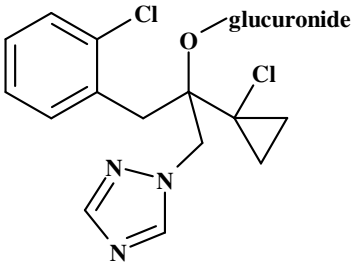
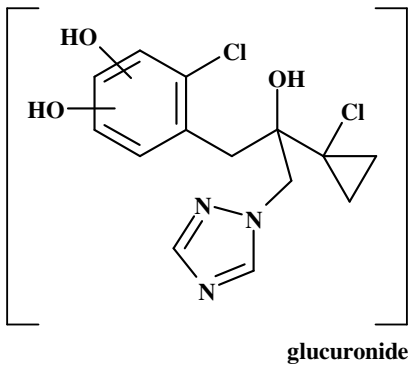
No.:	Structural formula	Name used in the summary CA index name [CAS#] if available Identified in metabolism or other studies
M47	 **glucoside**	JAU 6476-desthio-dihydroxy-diene-glucoside glucoside of M38 plant: peanut[a] [a] M47/M64
M48	 **glucoside**	JAU 6476-desthio-dihydroxy-glucoside glucoside of M34 plant: peanut[a] [a] M48/M57
M49	 **glucuronide**	JAU 6476-desthio-hydroxy-methoxy-glucuronide glucuronide of M28 animal: rat, goat
M50		JAU 6476-3,4-dihydroxy-diene animal: goat

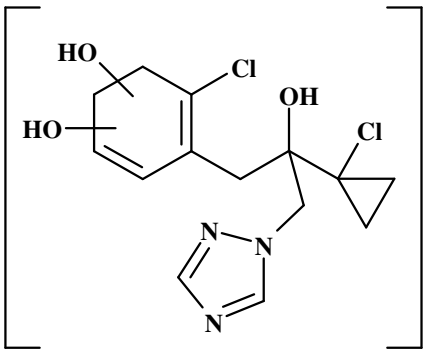
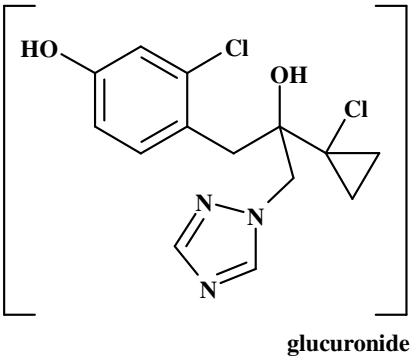
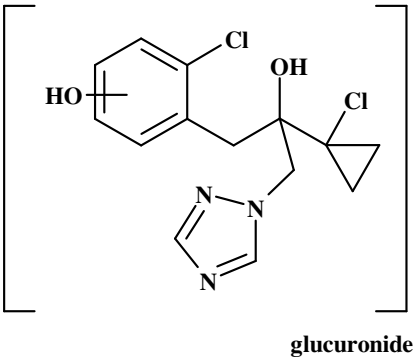
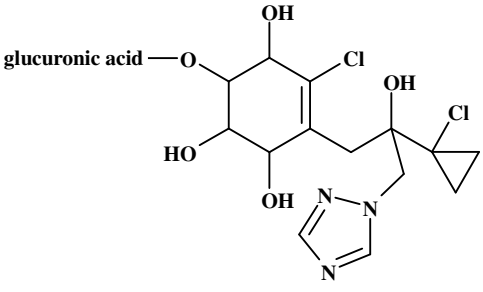
No.:	Structural formula	Name used in the summary CA index name [CAS#] if available Identified in metabolism or other studies
M51		JAU 6476-5,6-dihydroxy-diene animal: goat
M52	 **glucuronide**	JAU 6476-desthio-3,4-dihydroxy-dienyl-glucuronide glucuronide of M32 animal: goat, hen
M53	 **glucuronide**	JAU6476-desthio-5,6-dihydroxy-dienyl-glucuronide glucuronide of M41
M54	**malonic acid glucoside** 	JAU 6476-desthio–3-hydroxy-glucoside-malonic acid malonic acid glucoside of M14 plant: peanut[a], wheat[b] [a] M54/M55 [b] M54-M56

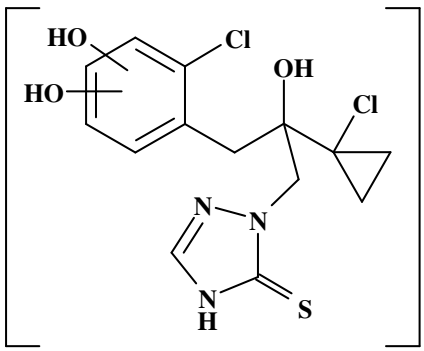
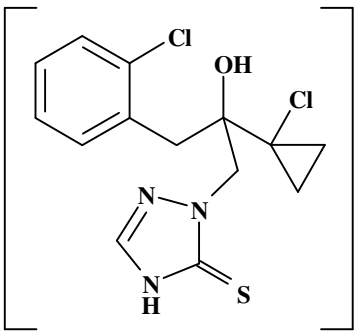
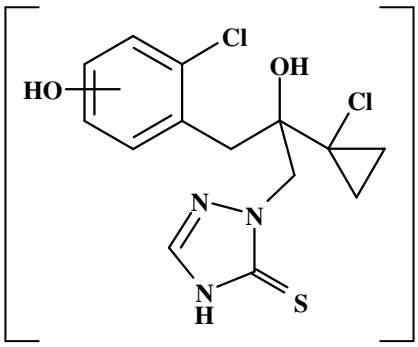
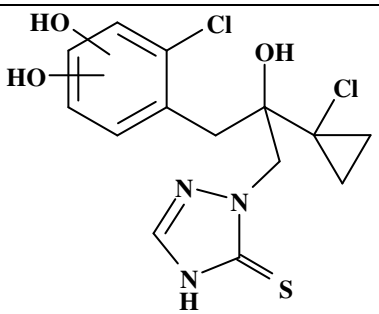
No.:	Structural formula	Name used in the summary CA index name [CAS#] if available Identified in metabolism or other studies
M55		JAU 6476-desthio-4-hydroxy-glucoside-malonic acid malonic acid glucoside of M15 plant: peanut[a], wheat[b] [a] M54/M55 [b] M54-M56
M56		JAU 6476-desthio-6-hydroxy-glucoside-malonic acid malonic acid glucoside of M17 plant: wheat
M57		JAU 6476-desthio-S-glucoside plant: peanut, hay[a] [a] M48/M57
M58		JAU 6476-desthio-α-hydroxy-glucoside glucoside of M18 plant: sugar beet[a], wheat[b] [a] mentioned in the pathway only [b] M04 as test substance

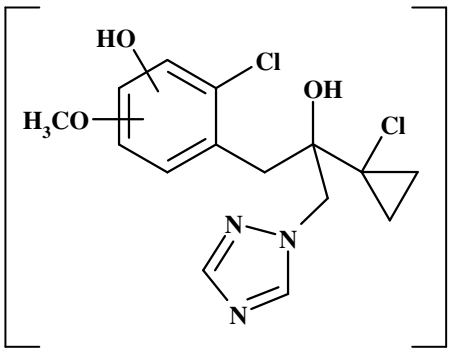
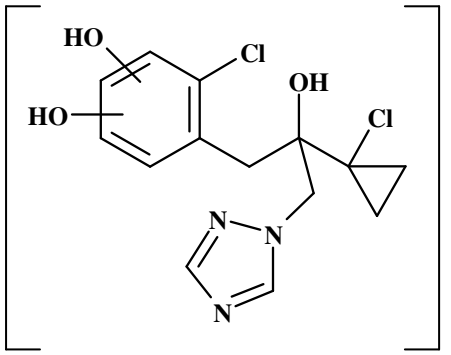
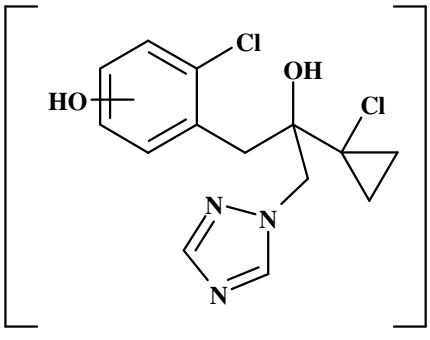
No.:	Structural formula	Name used in the summary CA index name [CAS#] if available Identified in metabolism or other studies
M59		JAU 6476-hydroxy-sulfonic acid glucoside plant: sugar beet , wheat
M60		JAU 6476-hydroxy-disulfonic acid glucoside plant: sugar beet*(200466[a])* [a] tentatively identified
M61		JAU 6476-triazolyl-sulfonic acid-ethanol
M62		JAU 6476-triazolyl-sulfonic acid-ethanol-glucoside glucoside of M61 plant: sugar beet
M63		JAU 6476-desthio-glucoside-malonic acid malonic acid glucoside of M04 plant: wheat

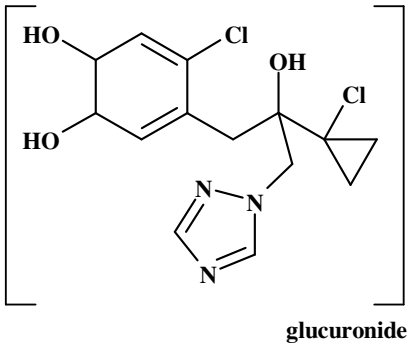
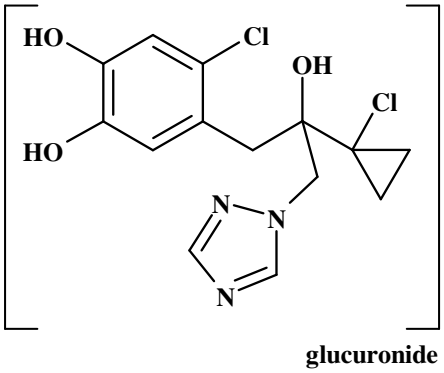
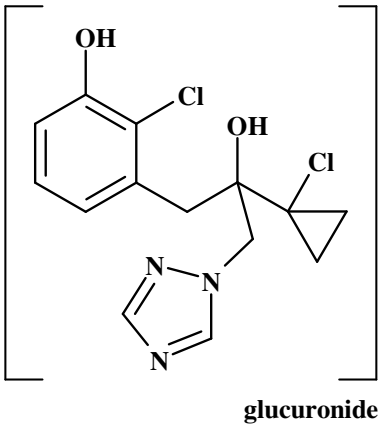
No.:	Structural formula	Name used in the summary CA index name [CAS#] if available Identified in metabolism or other studies
M64		JAU 6476-desthio-dihydroxy–olefin-glucoside glucoside of M27 plant: peanut rotational crop[a] [a] tentatively identified
M65		JAU 6476-desthio-dihydroxy-glucoside-malonic acid malonic acid glucoside of M34 plant: wheat
M66		Triazolyl-pyruvic acid plant: wheat[a] [a] postulated intermediate in the pathway only
M67		ß-glucoside of M04 plant: wheat[a] [a] M04 as test substance

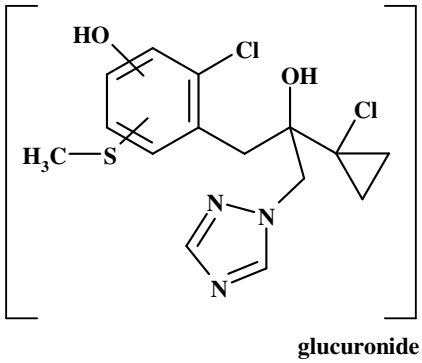
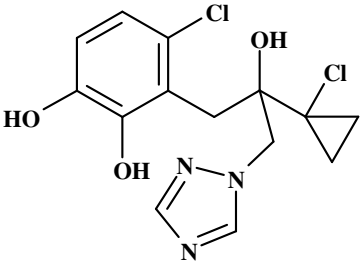
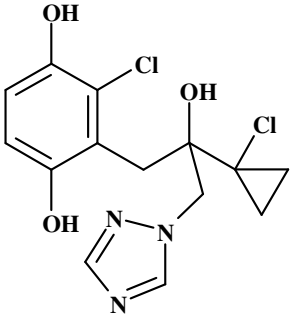
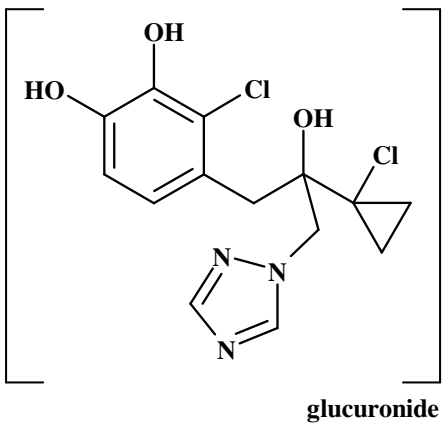
No.:	Structural formula	Name used in the summary CA index name [CAS#] if available Identified in metabolism or other studies
M68		JAU 6476-desthio-5-hydroxy-glucoside glucoside of M16 plant: wheat[a] [a] M21/M22/M23/M68
M69		JAU 6476-4-hydroxy-glucuronide glucuronide of M08 animal: goat
M70		JAU 6476-hydroxy animal: goat
M71		JAU 6476-desthio-glucuronide glucuronide of M04 animal: goat
M72		JAU 6476-desthio-dihydroxy-glucuronide glucuronide of M34 animal: rat, goat

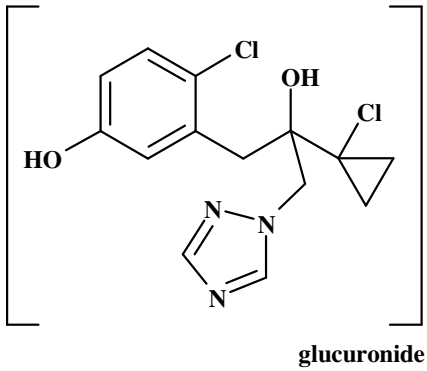
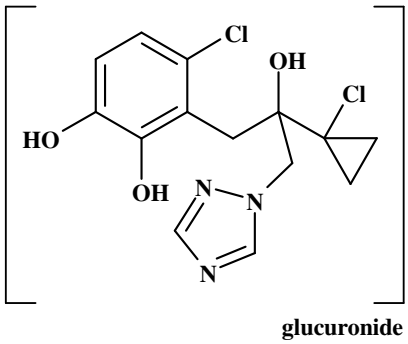
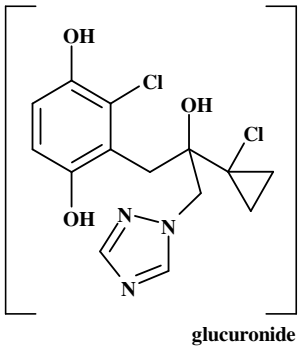
No.:	Structural formula	Name used in the summary CA index name [CAS#] if available Identified in metabolism or other studies
M73		JAU 6476-desthio-dihydroxy-dienyl-glucuronide glucuronide of M38 (M32 & M41 animal: rat, goat
M74		JAU 6476-desthio-4-hydroxy-glucuronide glucuronide of M15 animal: goat[a] [a] M04 as test substance
M75		JAU 6476-desthio-hydroxy-glucuronide glucuronide of M14/M15/M16/M17 animal: rat, goat
M76		JAU 6476-desthio-olefin-tetrahydroxy-glucuronide glucuronide of M39 animal: rat[a] [a] M04 as test substance

No.:	Structural formula	Name used in the summary CA index name [CAS#] if available Identified in metabolism or other studies
M77	 **glucuronide**	JAU 6476-dihydroxy-glucuronide glucuronide of M81 animal: goat
M78	 **lactoside**	JAU 6476-lactoside animal: goat
M79	 **sulfate**	JAU 6476-hydroxy-sulphate sulphate conjugate of M70 animal: goat
M80	SCN^-	Thiocyanate animal: goat, hen
M81		JAU 6476-dihydroxy

No.:	Structural formula	Name used in the summary CA index name [CAS#] if available Identified in metabolism or other studies
M82	 **sulfate**	JAU 6476-desthio-hydroxy-methoxy-sulphate sulphate conjugate of M28 animal: goat[a,b], hen[a] [a] M82/M83/M84 [b] M04 as test substance
M83	 **sulfate**	JAU 6476-desthio-dihydroxy-sulphate sulphate conjugate of M34 animal: goat[a,b], hen[a] [a] M82/M83/M84 [b] M04 as test substance
M84	 **sulfate**	JAU 6476-desthio-hydroxy-sulphate sulphate conjugate of M14/M15/M16/M17 animal: goat[a,b], hen[a] [a] M82/M83/M84 [b] M04 as test substance

No.:	Structural formula	Name used in the summary CA index name [CAS#] if available Identified in metabolism or other studies
M85		JAU 6476-desthio-4,5-dihydroxy-dienyl-glucuronide glucuronide of M36 animal: goat[a] [a] M04 as test substance
M86		JAU 6476-desthio-4,5-dihydroxy-glucuronide glucuronide of M35 animal: goat[a] [a] M04 as test substance
M87		JAU 6476-desthio-3-hydroxy-glucuronide glucuronide of M14 animal: goat[a] [a] M04 as test substance

No.:	Structural formula	Name used in the summary CA index name [CAS#] if available Identified in metabolism or other studies
M88		JAU 6476-desthio-hydroxy-S-methyl-glucuronide glucuronide of M37 animal: goat[a] [a] M04 as test substance
M89		JAU 6476-desthio-5,6-dihydroxy
M90		JAU 6476-desthio-3,6-dihydroxy
M91		JAU 6476-desthio-3,4-dihydroxy-glucuronide glucuronide of M33 animal: goat[a] [a] M04 as test substance

No.:	Structural formula	Name used in the summary CA index name [CAS#] if available Identified in metabolism or other studies
M92		JAU 6476-desthio-5-hydroxy-glucuronide glucuronide of M16 animal: goat[a] [a] M04 as test substance
M93		JAU 6476-desthio-5,6-dihydroxy-glucuronide glucuronide of M89 animal: goat[a,b] [a] test substance M04 [b] potential isomer
M94		JAU 6476-desthio-3,6-dihydroxy-glucuronide glucuronide of M90 animal: goat[a,b] [a] test substance M04 [b] potential isomer

Animal metabolism

The Meeting received animal metabolism studies with prothioconazole in rats, lactating goats and laying hens.

Prothioconazole is rapidly absorbed by all animals tested. It is excreted mainly via urine. The metabolites were similar in case of phenyl and triazole-labelled compounds. The metabolic pathway of prothioconazole follows two main routes:

- metabolic transformation reactions of the intact parent compound under conservation of the triazolinethione moiety
- transformation reactions after elimination of the sulphur from the triazolinthione moiety

The proposed metabolic pathway for goats and hens is shown in Figure 1. The major metabolites found in farm animals were also identified in the rat study.

Rats

Prothioconazole was rapidly and extensively (> 90%) absorbed following oral dosing. Excretion was mainly via urine and partly with faeces (Justus, K.; 2001, 2001a) and only 0.06% of the administered dose was eliminated via expired air. The metabolic pattern was similar between the phenyl and triazole labels, and the parent molecule remained largely intact. The major types of metabolic reactions identified were conjugation with glucuronic acid, oxidative hydroxylation of the phenyl moiety and desulphuration. Many metabolites were derived from JAU 6476-desthio *(M04)*. JAU 6476-S-glucuronide *(M06)*, JAU 6476-desthio *(M04)* and prothioconazole were the principal components in addition to ten minor metabolites identified in excreta.

Studies with metabolite M04, which is the major metabolite of prothioconazole in plants, revealed that about 18% of the administered dose occurred in faeces, and maximum 0.07% in urine (Koester, J; 2001, Klein, O, 1990).

Lactating goats

Livestock metabolism studies using phenyl (Weber, H and Spiegel, K; 2001) and triazole-labelled prothioconazole (Weber, E; Weber, H. and Spiegel, K; 2003, amended 2005)**,** and phenyl-labelled JAU 6476-desthio (*M04*) were conducted in the lactating goat. A metabolism study with phenyl-labelled JAU 6476-desthio *(M04)* was conducted (Weber, H; Weber E and Spiegel, K; 2002; Weber 2006) since the dominating residue in livestock feed items is the desthio-derivative of prothioconazole.

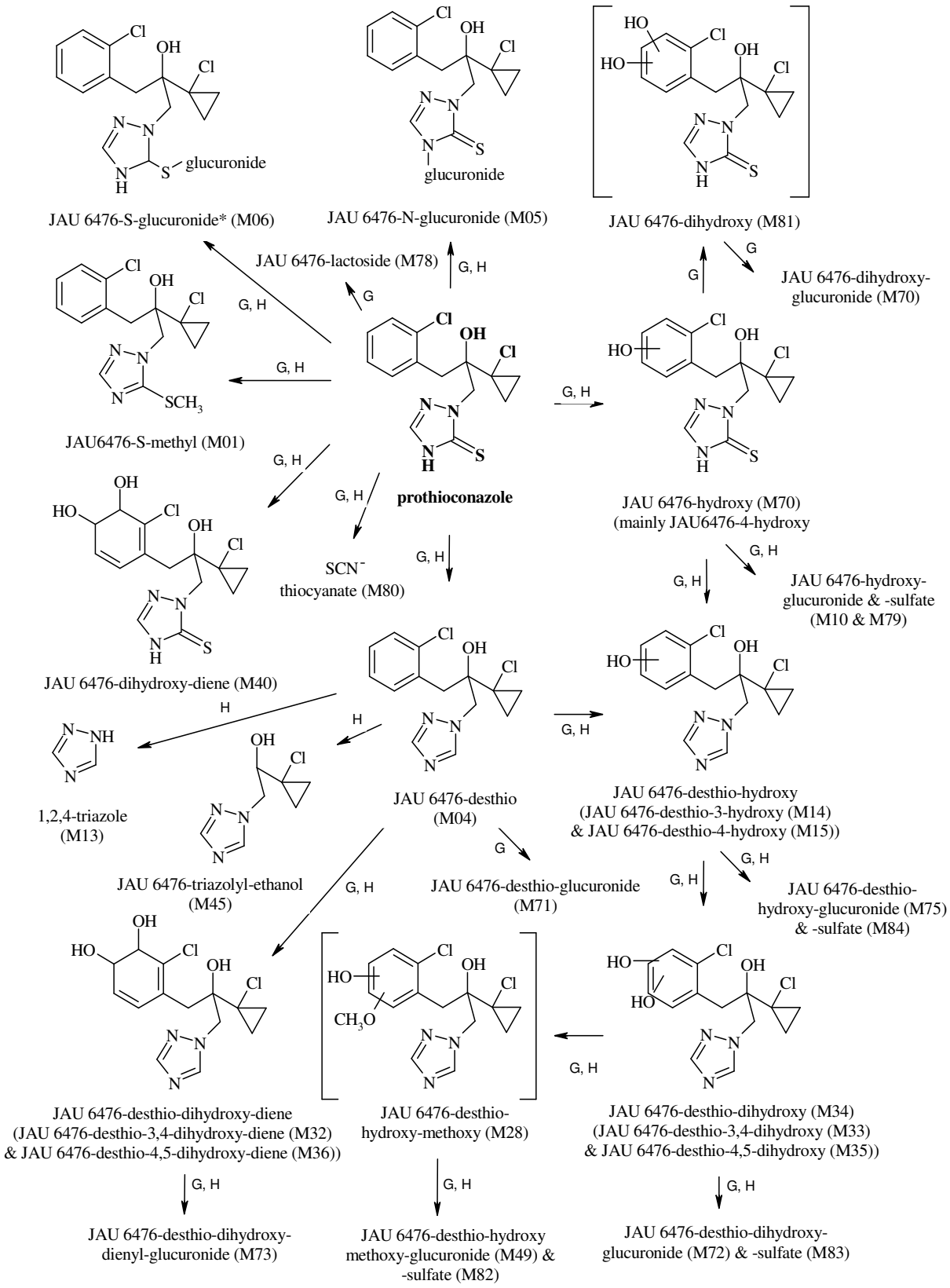
All studies followed the same design: Lactating goats of about 30–39 kg were three times orally dosed with radiolabelled test item (prothioconazole or JAU 6476-desthio) at a dose level of 10 mg/kg body weight/day. In each trial one goat received the doses on three consecutive days at intervals of 24 hours. The dose level for JAU 6476-desthio corresponded to 195 ppm test substance in feed.

Basic identification and quantification of prothioconazole and metabolites were performed within three months after sacrifice of the lactating goat.

Identification and analysis of metabolites

For analytical investigations, composites of muscle and fat were prepared. The milk samples collected at different time points were combined. The TRR values of the composite samples and the milk pool were determined.

Metabolite analyses were performed by HPLC as the primary method. Identification of metabolites was based on co-chromatography with authentic reference compounds (HPLC and/or HPTLC) or on spectroscopic evidence (HPLC-MS/MS and partly by ^{1}H-NMR).



G = goat; H = hen

Figure 1 Proposed metabolic pathway of prothioconazole in farm animals

Extractability of resides from milk, liver, muscle, kidney and fat ranged from 77% (fat) to 98% of the TRR (kidney). The identification rates (including the characterised polar metabolites) accounted for values between 49% and 78%. For milk, muscle and fat, the radioactivity remaining in the extracted solids accounted for less than 0.005 mg/kg for phenyl-labelled and 0.05 for triazole labelled compounds.

The animals were sacrificed 53 hours after the first and five hours after the last administration.

The mean recovery including excreta, milk, organs and tissues amounted to 68% of the total administered dose. An additional portion of radioactivity (about 32%) was assumed to be still present in the gastro-intestinal tract of the animals after sacrifice. TRR recovered in various samples during the study is shown in Table 1.

Table 1 Recovery of radioactivity after oral administration of 10 mg/kg bw phenyl- or triazole-labelled prothioconazole or phenyl-labelled JAU 6476-desthio (M04) to the lactating goat on three consecutive days

Biological material	Time after the first dose (h)	Administration no.	Values in percent of the totally administered radioactivity [a]		
			Phenyl	Triazole	Phenyl-M04
Urine (plus urine funnel rinsing)	0	1	–	–	–
	24	2	15.88	14.46	21.01
	48	3	17.44	15.44	22.99
	53	sacrifice	9.12	4.63	9.13
subtotal			42.44	34.53	53.13
Faeces	0	1	–	–	–
	24	2	9.92	10.14	8.15
	48	3	11.26	12.50	11.40
	53	sacrifice	2.97	1.58	1.12
subtotal			24.15	24.22	20.67
Milk	0	1	–	–	–
	8		0.004	0.005	0.012
	24	2	0.003	0.005	0.006
	32		0.004	0.008	0.011
	48	3	0.003	0.008	0.007
	53	sacrifice	0.003	0.006	0.010
subtotal			0.017	0.032	0.046
Totally excreted			66.61	58.78	73.85
Estimated residue in edible tissues			0.96	0.74	1.87
Recovery			67.57	59.52	75.72

[a]. test substances: Phenyl: Phenyl-ring labelled prothioconazole, Triazole: Triazole-ring labelled prothioconazole, M04: Phenyl-ring labelled JAU 6476-desthio

Storage stability investigations were conducted for liver and kidney as additional sample preparations became necessary during the identification process. For liver, a second and a third extraction was performed about 19 months and 28 months after sacrifice of the animal. In the case of kidney, the second extraction was conducted about 21 months after sacrifice. Comparison of metabolic profiles showed no significant change in the metabolite patterns; only a slight increase of the JAU 6476-desthio concentration was detected in both matrices.

Metabolic profile

The predominant portion of the total administered dose was found in excreta (58.8%–73.9%) and only in trace amounts in milk (0.02%–0.05%) and edible organs and tissues (0.96%–1.9%).

The radioactivity levels measured in the milk samples are recorded in Tables 2–4. The percentage values were calculated as a percentage of the sum of radioactivity administered.

Table 2 Radioactivity in the milk after oral administration of 10 mg/kg bw phenyl-labelled prothioconazole to the lactating goat on three consecutive days

Time after the first dosage (h)	Dosage no.	Concentration (µg ai equiv./mL)	% of the RA secreted per fraction	% of the RA summed up (cumulative)
0	1	–	–	–
8		0.042	0.004	0.004
24[a]		0.020	0.003	0.007
24	2	–	–	–
32		0.071	0.004	0.011
48[a]		0.026	0.003	0.014
48	3	–	–	–
53		0.061	0.003	0.017

[a] immediately prior to administration

Table 3 Radioactivity in the milk after oral administration of 10 mg/kg bw triazole-labelled prothioconazole to the lactating goat on three consecutive days

Time after the first dosage (h)	Dosage no.	Concentration (µg ai equiv./mL)	% of the RA secreted per fraction	% of the RA summed up (cumulative)
0	1	–	–	–
8		0.127	0.005	0.005
24[a]		0.080	0.005	0.010
24	2	–	–	–
32		0.242	0.008	0.018
48[a]		0.151	0.008	0.026
48	3	–	–	–
53		0.249	0.006	0.032

[a] immediately prior to administration

Table 4 Radioactivity in the milk after oral administration of 10 mg/kg bw phenyl-labelled JAU 6476-desthio to the lactating goat on three consecutive days

Time after the first dosage (h)	Dosage no.	Concentration (µg ai equiv./mL)	% of the RA secreted per fraction	% of the RA summed up (cumulative)
0	1	–	–	–
8		0.270	0.012	0.012
24[a]		0.074	0.006	0.018
24	2	–	–	–
32		0.282	0.011	0.029
48[a]		0.084	0.007	0.036
48	3	–	–	–
53		0.314	0.010	0.046

[a] immediately prior to administration

The mean recoveries of the total administered radioactivity in edible organs and tissues along with the corresponding concentrations are summarized in Tables 5 and 6.

Table 5 Residual radioactivity in the edible organs and tissues of the lactating goat after repeated (3×) oral administration of test substances[1] at a target dose of 10 mg/kg bw.

Tissue/organ	Concentration (mg ai equiv./kg)			% of the total RA administered		
	Phenyl	Triazole	M04)	Phenyl	Triazole	Phenyl M04
Liver	6.092	6.248	18.422	0.442	0.507	1.326
Kidney	6.762	4.507	18.986	0.067	0.053	0.180
Round muscle (sample)	0.084	0.115	0.277	–	–	–
Flank muscle (sample)	0.106	0.142	0.232	–	–	–
Loin muscle (sample)	0.100	0.115	0.232	–	–	–
Total body muscle[a]	0.097[b]	0.124[b]	0.247[b]	0.270	0.124	0.262
Peri-renal fat (sample)	0.162	0.112	0.216	–	–	–
Subcutaneous fat (sample)	0.149	0.109	0.233	–	–	–
Omental fat (sample)	0.172	0.213	0.240	–	–	–
Total body fat[a]	0.167[b]	0.145[b]	0.230[b]	0.180	0.057	0.097
Calculated/estimated residue in the edible tissues/organs				0.959	0.741	1.865

(Test substances: Phenyl: Phenyl-ring labelled prothioconazole, Triazole: Triazole-ring labelled prothioconazole, Phenyl M04: Phenyl-ring labelled JAU 6476-desthio).

[a] Calculated from the body weight; assuming 30% and 12% of the body weight for total body muscle and total body fat, respectively (body weight at sacrifice: 36.8 kg).

[b] Mean equivalent concentrations of the three different types of muscle or fat

There was no predominant metabolite detected in all matrices investigated, although some metabolites were present in all matrices: the parent compound prothioconazole was the main constituent in liver and prominent in muscle, kidney and fat (> 10% of TRR) but of minor importance in milk (< 1% of TRR). Metabolite JAU 6476-S-glucuronide (*M06*) was detected at high concentration levels in all matrices (> 10% of TRR).

A comparison of metabolites detected in the milk, tissue and organs of the lactating goat after administration of prothioconazole (phenyl- and triazole-label) is given in Table 6.

Table 6 Parent compound and metabolites in milk and tissues of the lactating goats administered with phenyl- and triazole-labelled prothioconazole in% of TRR and in mg ai eq/kg

Compound JAU 6476	Milk		Liver		Muscle		Kidney		Fat	
Label	Phe.	Triaz.	Phe.	Triaz.	Phe.	Triaz.	Phe.	Triaz.	Phe.	Triaz.
TRR (mg/kg)	0.037	0.150	6.092	6.248	0.088	0.117	6.762	4.507	0.169	0.174
prothioconazole *(ai)*	0.9	3.2	12.9	16.8	13.4	7.2	18.0	19.5	13.3	16.1
	< 0.001	*0.005*	*0.788*	*1.047*	*0.012*	*0.008*	*1.215*	*0.879*	*0.022*	*0.028*
Metabolites common to both labels										
-S-methyl (*M01*)				0.6						
				0.038						
-N-glucuronide *(M05)*	1.3		2.8	4.6	1.1		2.6	3.4	0.8	
	< 0.001		*0.170*	*0.284*	*0.001*		*0.179*	*0.155*	*0.001*	
-S-glucuronide *(M06)*	12.0	4.4	10.0	6.1	14.8	13.6	34.3	33.9	10.1	11.9
	0.004	*0.007*	*0.610*	*0.379*	*0.013*	*0.016*	*2.321*	*1.526*	*0.017*	*0.021*
-4-hydroxy (*M08*)		3.3	1.5	11.0		5.3		3.6		8.3

Compound JAU 6476	Milk		Liver		Muscle		Kidney		Fat	
Label	Phe.	Triaz.	Phe.	Triaz.	Phe.	Triaz.	Phe.	Triaz.	Phe.	Triaz.
TRR (mg/kg)	0.037	0.150	6.092	6.248	0.088	0.117	6.762	4.507	0.169	0.174
		0.005	*0.092*	*0.686*		*0.006*		*0.164*		*0.014*
-hydroxy-glucuronide (*M10*)		3.6	5.1	5.0	5.4	4.7	7.4	6.1	3.2	11.2
		0.005	*0.307*	*0.315*	*0.005*	*0.005*	*0.503*	*0.275*	*0.005*	*0.019*
-4-hydroxy-glucuronide (*M69*)			2.4		21.0	3.3	4.0	5.6	2.5	
			0.146		*0.002*	*0.004*	*0.271*	*0.250*	*0.004*	
-hydroxy-sulphate (*M79*)				6.5						
				0.408						
-lactoside *(M78)*		4.4								
		0.007								
-desthio *(M04)*	2.8	1.4	1.2	4.9	3.0	0.9	1.3	3.0	19.0	15.1
	0.001	*0.002*	*0.076*	*0.309*	*0.003*	*0.001*	*0.087*	*0.135*	*0.032*	*0.026*
-desthio-4-hydroxy (*M15*)			1.5	2.9						
			0.092	*0.179*						
group of M38, M40, M49, M74, M91 (dienes, glucuronides)	10.1									
	0.004									
group of M38, M52 (dienes, glucuronides)			6.4							
			0.392							
Metabolite specific to the triazole label:										
thiocyanate *(M80)*		41.1		2.0		29.6		9.0		12.4
		0.061		*0.128*		*0.035*		*0.406*		*0.022*
Total identified	29.2	61.3	53.6		44.7		70.8		52.4	
Total characterised	38.9	11.0	13.8		12.0		7.1		8.5	
Balance for extract	82.4	83.8	83.3	84.9	83.5	79.9	97.6	94.8	77.5	76.8
Solids	17.6	16.2	16.7	15.1	16.5	20.1	2.5	5.3	22.5	23.2
Solids (lactose)		10.8								
not analysed (loss)	14.3	0.7	15.9	3.2	26.9	4.5	19.7	2.6	16.6	1.8
Total balance	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0

% of TRR is printed in normal face; the mg/kg ai equivalent is printed with Italics.

M38 = JAU 6476-desthio-dihydroxy-diene

M40 = JAU 6476-dihydroxy-diene

M49 = JAU 6476-desthio-hydroxy-methoxy-glucuronide

M52 = JAU 6476-desthio-3,4-dihydroxy-dienyl-glucuronide

M74 = JAU 6476-desthio-4-hydroxy-glucuronide

M91 = JAU 6476-desthio-3,4-dihydroxy-glucuronide

In the study performed with JAU 6476-desthio *(M04)*, no predominant metabolite was detected for all matrices. Besides the test item, mainly conjugates of hydroxylated JAU 6476-desthio were identified. Since the metabolic patterns in the various matrices were quite complex, an additional

way for the characterisation of metabolites or metabolic groups was established by treating the extracts with boiling hydrochloric acid. The aim of the hydrolysis was to cleave conjugates and to convert non-aromatic compounds back into aromatic compounds with known structures. As a result, up to five relevant *marker compounds* were formed during acidic treatment. The majority of the metabolites could be traced back to the following compounds: JAU 6476-desthio (*M04*), JAU 6476-desthio-3-hydroxy (*M14*), JAU 6476-desthio-4-hydroxy (*M15*), JAU 6476-desthio-3,4-dihydroxy (*M33*), JAU 6476-desthio-4,5-dihydroxy (*M35*) and JAU 6476-desthio-glucuronide (*M71*). JAU 6476-desthio-glucuronide is an O-glucuronide which is not completely cleaved under the conditions chosen.

A comparison of the identified metabolites before and after treatment with boiling HCl is presented in Tables 7a–7f.

Table 7a JAU 6476-desthio: Quantitative evaluation of the metabolites before and after acid treatment of goats' milk

Before hydrolysis	% of TRR	mg/kg	After treatment with 5N HCl (100 °C for 4 h)	% of TRR	mg/kg
JAU 6476-desthio-			JAU 6476-desthio-		
-3,4-dihydroxy-dienyl-glucuronide[a]	5.4	0.016	-glucuronide	5.1	0.015
-3,4-dihydroxy-diene[a]	5.5	0.016	-desthio -3,4-dihydroxy[c]	31.1	0.089
-3-hydroxy-glucuronide[b] -3,4-dihydroxy-glucuronide[c] -4,5-dihydroxy-glucuronide[b]	2.6	0.008	-4,5-dihydroxy	17.7	0.051
			-3-hydroxy	11.0	0.031
-glucuronide	6.2	0.018	-4-hydroxy	19.7	0.056
-4-hydroxy-glucuronide[b] -hydroxy-methoxy-glucuronide[b]	5.1	0.015			
-3,4,-dihydroxy[c]	1.6	0.004			
-4,5-dihydroxy[b]	1.4	0.004			
Sulphate conjugates of -hydroxy isomers, -dihydroxy isomers, -hydroxy-methoxy	44.0	0.126			
Sum identified	58.1	0.166	Sum identified	84.6	0.242
Sum tentatively. identified	13.7	0.039			
Totally identified	71.8	0.205	Totally identified	84.6	0.242
Sum characterised	16.7	0.048	Sum characterised	3.9	0.011
number of characterised metabolites	5		number of characterised metabolites	1	

[a] two diastereomers

[b] tentative identification

[c] unambiguous structure assignment by 1H-NMR spectroscopy

Table 7b JAU 6476-desthio: Quantitative evaluation of the metabolites before and after acid treatment of goat liver

Before acid hydrolysis	% of TRR	mg/kg	After treatment with 5N HCl (100 °C for 4 h)	% of TRR	mg/kg
JAU 6476-desthio-			JAU 6476-desthio-		
-3,4-dihydroxy-dienyl-glucuronide[a]	5.8	1.069	-3,4-dihydroxy[c]	5.3	0.983
-3,4-dihydroxy-diene[b]	1.2	0.213	-4,5-dihydroxy[d]	2.1	0.390
-3-hydroxy-glucuronide[b]	2.7	0.504	-3-hydroxy	4.6	0.850
-4-hydroxy-glucuronide[b] -hydroxy-methoxy-glucuronide[b]	2.8	0.511	-4-hydroxy	10.2	1.884
			JAU 6476-desthio	36.1	6.653

Before acid hydrolysis	% of TRR	mg/kg	After treatment with 5N HCl (100 °C for 4 h)	% of TRR	mg/kg
JAU 6476-desthio-			JAU 6476-desthio-		
-3,4-dihydroxy[c]	2.2	0.396			
-4,5-dihydroxy[d]	4.8	0.878			
-3-hydroxy	1.0	0.178			
-4-hydroxy	8.4	1.542			
parent compound (JAU 6476-desthio)	31.2	5.744			
Sum identified	53.2	9.805	Sum identified	58.4	10.760
Sum tentatively. identified	6.7	1.227			
Totally identified	59.9	11.033	Totally identified	58.4	10.760
Sum characterised	11.0	2.024	Sum characterised	12.5	2.296
number of characterised metabolites	9		number of characterised metabolites	10	

[a] two diastereomers

[b] tentative identification (identified with primary method, no confirmation with secondary method)

[c] unambiguous structure assignment by 1H-NMR spectroscopy

[d] co-elution with JAU 6476-desthio-glucuronide possible

Table 7c JAU 6476-desthio: Quantitative evaluation of the metabolites before and after acid treatment of goat kidney

Before acid hydrolysis	% of TRR	mg/kg	After treatment with 5N HCl (100 °C for 4 h)	% of TRR	mg/kg
JAU 6476-desthio-			JAU 6476-desthio-		
-3,4-dihydroxy-dienyl-glucuronide[a)]	21.0	3.992	-3,4-dihydroxy	4.2	0.802
-3,4-dihydroxy-diene[a]	1.6	0.307	-4,5-dihydroxy	2.3	0.444
-4,5-dihydroxy-glucuronide[b] -3-hydroxy-glucuronide[b]	4.9	0.933	-3-hydroxy	22.7	4.303
			-4-hydroxy	17.1	3.236
-4-hydroxy-glucuronide[b] -hydroxy-methoxy-glucuronide[b]	7.3	1.388	-glucuronide	14.2	2.700
			JAU 6476-desthio	19.0	3.595
-glucuronide	24.1	4.567			
-3-hydroxy	1.2	0.231			
-4-hydroxy	4.1	0.770			
parent compound (JAU 6476-desthio)	7.7	1.454			
Sum identified	58.0	11.013	Sum identified	79.5	15.080
Sum tentatively. identified	13.9	2.628			
Totally identified	71.9	13.641	Totally identified	79.5	15.080
Sum characterised	14.5	2.750	Sum characterised	6.9	1.311
number of characterised metabolites	6		number of characterised metabolites	4	

[a] two diastereomers

[b] tentative identification

Table 7d JAU 6476-desthio: Quantitative evaluation of the metabolites before and after acid treatment of goat muscle

Before acid hydrolysis	% of TRR	mg/kg	After treatment with 5N HCl (100 °C for 4 h)	% of TRR	mg/kg
JAU 6476-desthio-			JAU 6476-desthio-		
-3,4-dihydroxy-diene-glucuronide[a]	20.9	0.056	-3,4-dihydroxy[c]	8.6	0.023
-3,4-dihydroxy-diene[a]	10.8	0.029	-4,5-dihydroxy	2.4	0.006
-3,4-dihydroxy-glucuronide[c]	5.9	0.016	-3-hydroxy	35.1	0.093
-glucuronide[d]	3.6	0.009	-4-hydroxy	18.5	0.049
-4-hydroxy-glucuronide[b]	5.8	0.016	-glucuronide	1.5	0.004
-hydroxy-methoxy-glucuronide[b]	5.2	0.014	parent compound (JAU 6476-desthio)	2.9	0.008
-3,4-dihydroxy[c]	1.7	0.005			
-4,5-dihydroxy	2.8	0.007			
-3-hydroxy	4.8	0.013			
-4-hydroxy	3.0	0.008			
parent compound (JAU 6476-desthio)	1.8	0.005			
Sum identified	49.4	0.131	Sum identified	68.9	0.183
Sum tentatively. identified	16.9	0.045			
Totally identified	66.3	0.176	Totally identified	68.9	0.183
Sum characterised	10.7	0.029	Sum characterised	8.1	0.021
number of characterised metabolites	4		number of characterised metabolites	4	

[a] two diastereomers

[b] tentative identification (identified with primary method, no confirmation with secondary method)

[c] unambiguous structure assignment by 1H-NMR spectroscopy

[d] co-elution with JAU 6476-desthio-glucuronide possible

Table 7e JAU 6476-desthio: Quantitative evaluation of the metabolites before and after acid treatment of goat fat

Before acid hydrolysis	% of TRR	mg/kg	After treatment with 5N HCl (100 °C for 4 h)	% of TRR	mg/kg
JAU 6476-desthio-			JAU 6476-desthio-		
-3,4-dihydroxy-diene-glucuronide[a]	22.9	0.053	-3,4-dihydroxy[c]	6.8	0.016
-3,4-dihydroxy-diene[b]	4.3	0.010	-4,5-dihydroxy	2.3	0.005
-4,5-dihydroxy-glucuronide[b] -3-hydroxy-glucuronide[b]	5.3	0.012	-3-hydroxy	28.9	0.067
			-4-hydroxy	21.1	0.049
-4-hydroxy-glucuronide[b]	4.7	0.011	-glucuronide	2.3	0.005
-glucuronide -hydroxy-methoxy-glucuronide[b]	4.2	0.010	JAU 6476-desthio	12.3	0.028
-3,4-dihydroxy[c]	5.4	0.012			
-4-hydroxy[d]	14.6	0.034			
parent compound (JAU 6476-desthio)	13.9	0.032			
Sum identified	60.8	0.141	Sum identified	73.7	0.170
Sum tentatively. identified	14.3	0.033			
Totally identified	75.1	0.174	Totally identified	73.7	0.170

Before acid hydrolysis	% of TRR	mg/kg	After treatment with 5N HCl (100 °C for 4 h)	% of TRR	mg/kg
JAU 6476-desthio-			JAU 6476-desthio-		
Sum characterised	9.0	0.021	Sum characterised	10.5	0.024
number of characterised metabolites	2		number of characterised metabolites	3	

[a] two diastereomers

[b] tentative identification (identified with primary method, no confirmation with secondary method)

[c] unambiguous structure assignment by 1H-NMR spectroscopy

[d] co-elution with JAU 6476-desthio-glucuronide possible

The hydroxylation positions of JAU 6476-desthio-3,4-dihydroxy and of its corresponding glucuronic acid conjugate were assigned unambiguously in an additional study (Weber, 2006). The metabolites described as JAU 6476-desthio-dihydroxy *(M34)* and JAU 6476-desthio-dihydroxy-glucuronide (*M72*) in all farm animal studies were assigned retrospectively to JAU 6476-desthio-3,4-dihydroxy *(M33)* and JAU 6476-desthio-3,4-dihydroxy-glucuronide *(M91)*. The following table summarizes the occurrence of major metabolites in milk and tissues.

Table 7f Major metabolites detected in lactating goat after administration of phenyl-labelled JAU 6476-desthio *(M04)*

	Milk		Liver		Muscle		Kidney		Fat	
TRR[a] (mg/kg) =	*0.286*		*18.421*		*0.266*		*18.975*		*0.231*	
	% TRR	mg/kg	% TRR	mg/kg	% TRR	mg/kg	% TRR	mg/kg	% TRR	mg/kg
Major identified components										
JAU 6476-desthio *(M04)*			31.2	5.744	1.8	0.005	7.7	1.454	13.9	0.032
JAU 6476-desthio-glucuronide *(M71)*	6.2	0.018			3.57[e]	0.009	24.1	4.567	4.2	0.010
JAU 6476-desthio-3,4-dihydroxy-diene (*M32*)[b]	5.5	0.016	1.2	0.213	10.8	0.029	1.6	0.307	4.3	0.010
JAU 6476-desthio-3,4-dihydroxy-dienyl-glucuronide (*M52*)[b]	5.4	0.016	5.8	1.069	20.9	0.056	21.0	3.992	22.9	0.053
sulphate conjugates[c]	44.0	0.126								
Minor identified components (sum of 8 comp. in minimum)	10.7	0.031	14.8	4.009	27.6	0.079	17.5	3.322	24.5	0.069
Total identified	58.1	0.166	53.2	9.805	49.4	0.131	58.0	11.013	60.8	0.141
Total tentatively identified[d]	13.7	0.039	6.7	1.227	16.9	0.045	13.9	2.628	14.3	0.033
Total characterised	16.7	0.048	11.0	2.024	10.7	0.029	14.5	2.750	9.0	0.021
Fractions not analysed	5.6	0.016	10.7	1.965	11.8	0.031	10.8	2.053	4.4	0.010
Extractable	94.1	0.269	81.6	15.023	88.8	0.236	97.2	18.444	88.6	0.205
Unextractable/ Solids	5.9	0.017	18.5	3.398	11.2	0.030	2.8	0.531	11.5	0.026

[a] TRR determined by combustion analysis after homogenization and pooling (if applicable) of the sample

[b] Sum of two diastereomers

[c] Sulphate conjugates of JAU 6476-desthio-hydroxy, JAU 6476-desthio-dihydroxy, JAU 6476-desthio-hydroxy-methoxy (*M84, M83, M82*)

[d] only one chromatographic method employed or co-elution with another compound in the confirmatory method

[e] co-elution with JAU 6476-desthio-hydroxy- (*M75*) and JAU 6476-desthio-dihydroxy-glucuronide (*M72*) is possible

The presence of triazole derivatives or free 1,2,4-triazole was excluded in each matrix under investigation. An additional recovery experiment for 1,2,4-triazole in milk showed that amounts of at least 0.05 mg ai. eq/kg could be detected easily by TLC after sample preparation. Free 1,2,4-triazole (as well as the polar metabolites thiocyanate and possible triazole derivatives) were separated from the other less polar metabolites with the help of an XAD 7 column. TLC analysis of the flow-through fraction of the column showed that a spiked amount of about 0.05 mg/kg could be detected without any problems. Thus, the recovery experiment guaranteed that 1,2,4-triazole can be detected down to a level of at least 0.05 mg ai. eq/kg (corresponding to approx. 0.01 mg/kg triazole). If triazole had been present in milk, organs or tissues at that level or at higher levels it would have been detected.

Laying hens

The studies with phenyl-labelled prothioconazole (Weber H and Spiegel, K, 2001a) and triazole-labelled prothioconazole (Weber, H and Justus, K 2003) followed the same design. Six white leghorn laying hens of about 1.5–1.6 kg were orally dosed with radio-labelled prothioconazole at a dose level of 10 mg/kg body weight. The hens received the doses on three consecutive days in intervals of 24 h. Eggs were collected once a day. The animals were sacrificed five hours after the last administration.

Tissues collected and analysed were: liver (whole organ), kidney (whole organ), eggs from ovary/oviduct, muscles (leg muscle and breast muscle), fat (subcutaneous fat), and skin (without subcutaneous fat). The analyses were performed within three months after sacrifice.

The TRR values in the homogenised pools were determined. All samples and extracts were stored at –≤ 18 °C.

The metabolite profile in the extracts was determined by reversed phase HPLC using ^{14}C-flow-through detection as the primary analytical method. Identification of metabolites was based on the HPLC profiles of the hen liver. The liver metabolites of hen were assigned based on the comparison of the HPLC profile with the HPLC liver profile of the corresponding prothioconazole goat study (Weber and Spiegel, 2001).

The extractability of the TRR was high for all tissues and ranged from 77% for eggs to 98% for fat.

The mean recovery including excreta, eggs, organs and tissues amounted to 79% of the total administered dose of phenyl-labelled prothioconazole. Due to the relatively short survival period after the last dosage, the missing amount of about 21%was not determined in the excreta. Taking the low quantities of radioactivity in muscle and fat into account, the authors assumed that the missing portion (21%) of the radioactivity was most probably present in the gastrointestinal tract at sacrifice.

The predominant portion of the total administered dose was found in excreta (66% for triazole and 78% for phenyl-labelled prothioconazole), and only trace amounts were detected in eggs (0.01%) and edible organs and tissues (about 0.9%). The TRR% and the concentration (mg ai eq/kg) of parent compound and metabolites in eggs, tissue and organs of laying hens after oral administration of phenyl- and triazole-labelled prothioconazole are summarized in Table 8.

Table 8 Parent compound and metabolites in eggs, tissue and organs of laying hens after oral administration of phenyl- and triazole-labelled prothioconazole (in % of TRR and in mg ai eq/kg)

Compound	Liver		Egg		Muscle		Fat	
JAU 6476-	% TRR		% TRR		% TRR		% TRR	
Label	phenyl	triazole	phenyl	triazole	phenyl	triazole	phenyl	triazole
TRR (mg ai equiv./kg)[f]	4.017	3.531	0.036	0.050	0.089	0.122	0.450	0.290
Prothioconazole (JAU 6476)	24.8	30.7	3.6	3.4	11.3	2.5	30.3	15.9
	0.995	1.085	0.001	0.002	0.010	0.003	0.137	0.046
Metabolites common to both labels:								
JAU 6476-S-methyl (M01)	2.2	1.7	1.9	1.2	6.4	2.2	19.6	28.5

Compound	Liver		Egg		Muscle		Fat	
JAU 6476-	% TRR		% TRR		% TRR		% TRR	
Label	phenyl	triazole	phenyl	triazole	phenyl	triazole	phenyl	triazole
TRR (mg ai equiv./kg)[f]	4.017	3.531	0.036	0.050	0.089	0.122	0.450	0.290
	0.090	0.059	0.001	0.001	0.006	0.003	0.088	0.083
JAU 6476-N-glucuronide (M05)	1.1[d]	0.2			0.6[d]			
	0.043[d]	0.006			0.001[d]			
JAU 6476-S-glucuronide (M06)[e]	11.9[a]	14.9[a]	17.0	23.7[b]	15.5	9.8	5.3	7.2
	0.479[a]	0.526[a]	0.006	0.012[b]	0.014	0.012	0.024	0.021
JAU 6476-4-hydroxy (M08)	0.7[d]	0.3			1.6[d]			
	0.029[d]	0.011			0.001[d]			
JAU 6476-hydroxy-glucuronide (M10)	2.6							
	0.103							
JAU 6476-dihydroxy-diene (M40)	0.9[d]				1.3[d]			
	0.035[d]				0.001[d]			
JAU 6476-desthio (M04)	4.2	4.9	20.1	6.2	7.2	2.1	29.0	26.8
	0.167	0.172	0.007	0.003	0.006	0.003	0.130	0.078
JAU 6476-desthio-4-hydroxy (M15)	2.7	0.9	3.3[d]					
	0.109	0.031	0.001[d]					
JAU 6476-desthio-hydroxy-sulphate (M84)	3.3	1.6						
	0.131	0.055						
JAU 6476-desthio-3,4-dihydroxy-dienyl-glucuronide (M52)	2.3				0.6[d]			
	0.092				0.001[d]			
JAU 6476-desthio-hydroxy-methoxy-sulphate (M82), JAU 6476-desthio-dihydroxy-sulphate (M83) and JAU 6476-desthio-hydroxy-sulphate (M84)	7.8	11.9			1.5			0.7
	0.314	0.419			0.001			0.002
Metabolites specific to the triazole label:								
1,2,4-triazole (M13)		1.0		11.4		18.7		1.5[c]
		0.037		0.006		0.023		0.004[c]
JAU 6476-triazolyl-ethanol (M45)		3.6		15.6		28.3		1.6
		0.129		0.008		0.035		0.005
thiocyanate (M80)		0.7		9.8		4.0		1.5[c]
		0.023		0.005		0.005		0.004[c]
Total identified	61.7	72.3	42.6	71.4	41.9	67.6	84.1	82.3
Total characterised	10.6	12.0	10.4	10.4	11.7	11.3	-	5.9
Solids	20.8	12.7	22.9	15.7	19.4	18.9	2.6	2.1
not analysed (loss)	6.8	1.9	24.1	2.5	26.9	2.2	13.3	9.7
Total balance	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0

[a] may contain a trace amount of JAU 6476-desthio-3-hydroxy *(M14)*

[b] may contain a minor amount of JAU 6476-desthio-4-hydroxy *(M15)* and a trace amount of JAU 6476-desthio-3-hydroxy *(M14)*

[c] for the fat the values of 1,2,4-triazole *(M13)* and thiocyanate *(M80)* could only be determined as the sum of both

metabolites

[d] identification by HPLC only, no or no unambiguous confirmation by HPTLC (= characterised peak)

[e] position of conjugation was unassigned in the study with the phenyl-label, but a retrospective identification followed in the goat study by spectroscopic evidence (Weber et al.; 2003, amended 2005,)

[f.] measured by a combustion analysis of an aliquot from the pooled samples

The concentrations (mg ai eq/kg) in the dissected tissues and organs of individual laying hens at the time of sacrifice, 53 hours after the first administration of the phenyl-labelled prothioconazole are shown in Tables 9 and 10.

Table 9 TRR concentrations [a] (mg ai eq/kg) in the dissected tissues and organs of individual laying hens at the time of sacrifice, 53 hours after the first administration of 10 mg/kg phenyl-labelled prothioconazole

Tissue/organ	Animal no.							
	586	587	588	589	590	591	Mean	CV %[b]
Liver	5.211	2.858	4.187	2.934	3.883	5.414	4.081	26.7
Kidney	4.214	3.683	5.242	3.721	3.863	6.501	4.537	24.8
Eggs from ovary/oviduct	0.642	0.496	0.496	0.494	0.819	0.634	0.597	21.7
Muscle, leg	0.137	0.068	0.103	0.081	0.114	0.137	0.107	26.9
Muscle, breast	0.071	0.038	0.058	0.043	0.059	0.078	0.058	26.6
Skin without subcutaneous fat	0.501	0.251	0.403	0.318	0.384	0.441	0.383	23.1
Fat, subcutaneous	0.387	0.253	0.449	0.311	0.470	0.730	0.433	38.6

[a] values for single samples together with the calculated arithmetic mean.

[b] coefficient of variation in percent

Table 10 TRR concentrations (mg ai eq/kg) in the dissected tissues and organs of individual laying hens at the time of sacrifice, 53 h after the first administration of 10 mg/kg triazole labelled prothioconazole

Tissue/organ	Animal no.							
	447	448	449	450	451	452	Mean	CV %[a]
Liver	3.281	4.112	4.129	3.355	3.259	2.548	3.447	17.3
Kidney	2.973	3.664	4.417	2.885	3.127	3.220	3.381	17.0
Eggs from ovary/oviduct	0.626	0.681	0.480	0.898	0.597	0.455	0.623	25.8
Muscle, leg	0.121	0.236	0.144	0.133	0.110	0.089	0.139	37.1
Muscle, breast	0.099	0.125	0.103	0.098	0.082	0.071	0.096	19.1
Skin without subcutaneous fat	0.263	0.373	0.315	0.342	0.307	0.249	0.308	15.3
Fat, subcutaneous	0.214	0.399	0.371	0.377	0.404	0.289	0.342	22.0

[a] coefficient of variation in percent

The mean concentrations in eggs, collected within a 24 h period after each administration, are presented in Table 11. The overall level of residues in eggs was low. The highest mean concentration was found in the eggs collected during the last sampling period (48–53 h after the first dosage).

Table 11 Mean values of TRR concentrations (mg ai eq/kg) in the eggs of laying hens after oral administration of 10 mg/kg bw on three consecutive days

Test no.	Time after the first dosage (h)	Administration no.	Concentration (mg ai eq/kg)	
			Phenyl	Triazole
1	0	1	–	–
	24	2	0.004	0.001
	48	3	0.029	0.066
	53	–	0.086	0.104

Plant metabolism

The Meeting received studies on wheat, peanut, and sugar beets following foliar application and seed treatment.

Prothioconazole is extensively metabolised and the most important pathways for metabolism are common to all crops. The proposed metabolic pathway of prothioconazole summarising the metabolism in the various crops, including confined rotational crops, is shown in Figure 2.

Wheat

The metabolism of prothioconazole has been investigated with both positions of radiolabel following application as a foliar treatment, and after seed dressing. The metabolism of JAU 6476-desthio *(M04)* following spray application was also studied.

Study 1 with [phenyl-UL-^{14}C]prothioconazole formulated as EC 250 was carried out on spring wheat planted in sandy loam soil placed in a 1 m^2 container (Haas, M and Bornatsch, W; 2000). The test material was applied twice at a rate of 0.22 kg/ha to wheat plants at the beginning of tillage (growth stage of the BBCH-32, node 2 at least 2 cm above node 1) and at full flowering (BBCH 65). The plants were grown under environmental conditions (sunlight and temperatures). A glass roof protected the plants from rainfall. The soil was surface irrigated.

The green material was first sampled six days after the second application at the early hay stage. A hay sample was collected 26 days after the second application at early dough stage and mature ears were harvested 48 days after the second application by separating them from the stalks. Wheat plants were cut at soil surface level and combined with the chaff.

Study 2 with [triazole-3,5-^{14}C]prothioconazole formulated as SC 480 was conducted on spring wheat planted in sandy loam soil placed in a 2 m^2 stock tub (Duah, FK and Lopez, RT, 2004). The wheat was treated with 178 g ai/ha at BBCH crop growth stages 32 and with 292 g as/ha at BBCH 65. One day after application, the soil tub was moved to the outside of the greenhouse.

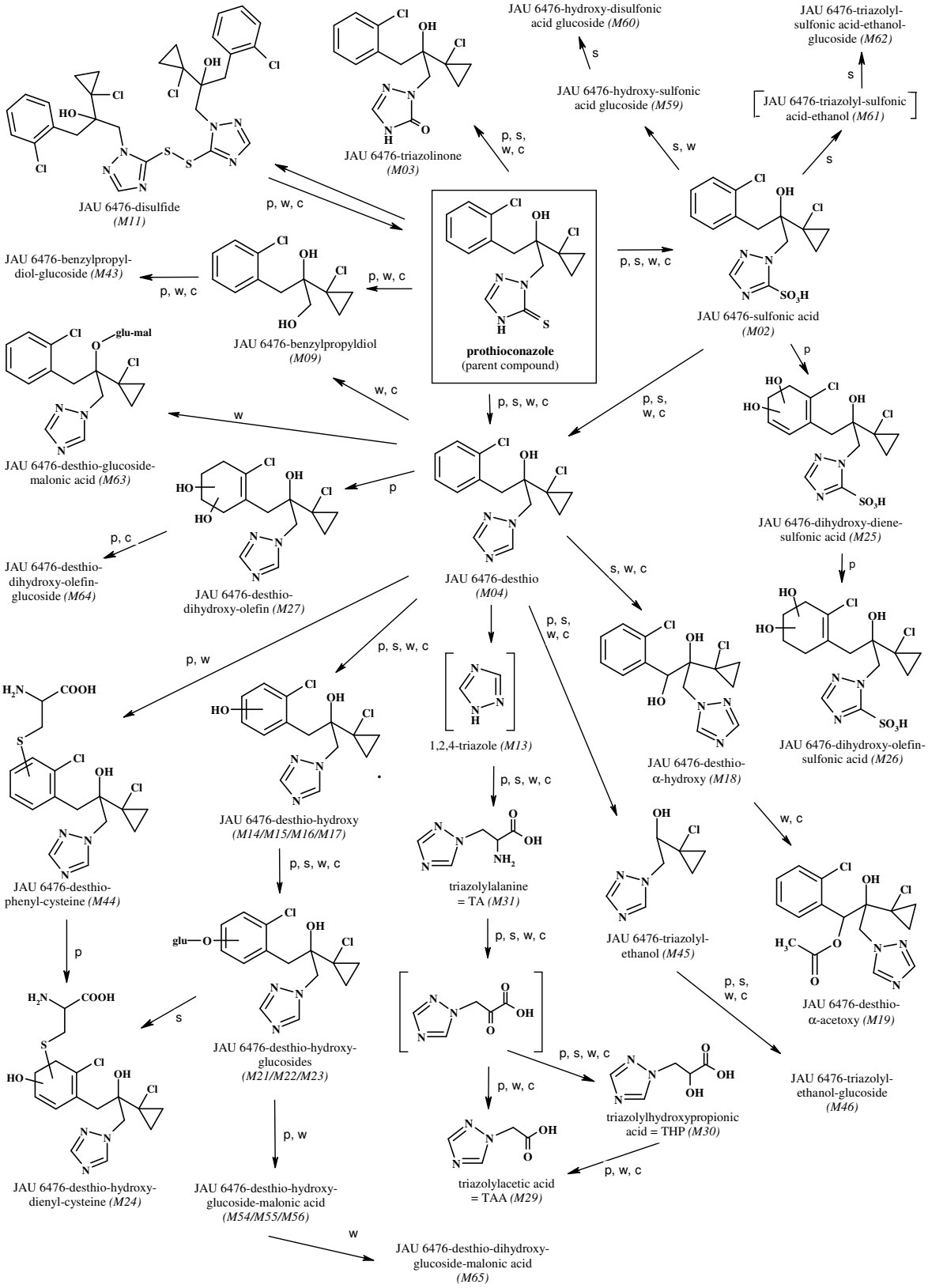


Figure 2Proposed metabolic pathway of prothioconazole in plants

p = peanuts, s = sugar beets, w = wheat, c = confined rotational crop

The samples of wheat forage, hay, straw and grain were harvested according to normal farming practice (forage at the end of tillage, hay at the early to medium milk stage, straw and grain at

maturity). Wheat hay was allowed to dry in the greenhouse for approximately three days prior to further processing.

Study 3 using [phenyl-UL-^{14}C]prothioconazole was conducted with wheat seeds treated at rates of 20 g active substance/100 kg seeds (1× experiment) and 100 g /100 kg seed (5× experiment). The test substance was dissolved in pure acetonitrile for seed dressing (Haas, M, 2001a).

The green material, hay and ripe heads were harvested at 57 days (BBCH stage 41), 110 days (BBCH 83) and 153 days after seed dressing, respectively.

In all studies the measurement of the radioactivity in the various samples was carried out by liquid scintillation counting (LSC). Post extraction solids containing radioactivity were combusted in an oxygen atmosphere. The released $^{14}CO_2$ was trapped in an alkaline scintillation cocktail and radioassayed by LSC.

The total radioactive residues (TRRs) in forage, hay, straw and grain of wheat were determined by summation of the extracted radioactivity in the acetonitrile/water extracts plus radioactivity remaining in the solids and were expressed as mg ai eq/kg sample material.

Identification and quantification

The profile and quantitative evaluation of radioactivity (metabolite profile) in the aqueous and organic extracts was determined by TLC. Identification of metabolites was based on isolated and identified straw metabolites or on co-chromatography with reference compounds. The metabolites of wheat straw were identified by HPLC-MS/MS and if possible by ^{1}H-NMR after isolation of the compound by HPLC.

Storage stability

The storage stability of parent compound and metabolites of wheat forage, hay, straw and grain samples, which were stored under freezer conditions at –18 °C or below, was checked at different dates in progress of the experimental work. The results of the storage stability analysis were virtually the same as those for the metabolism experiments and no significant changes in the metabolic pattern had occurred during a storage period of more than two years.

The total radioactive residue (TRR) values of forage, hay, straw and grain in all three wheat metabolism studies with prothioconazole are summarised in Table 12.

Table 12 Total radioactive residues (TRR) as mg/kg parent equivalent, in wheat following spray application with phenyl- and triazole labelled prothioconazole

Matrix	TRR (mg/kg parent equivalent) following application of prothioconazole as			
	Foliar treatment		Seed dressing	
	Phenyl-label	Triazole-Label	Phenyl-label	
			1× experiment	5× overdose experiment
forage	10.45	7.96	0.020	0.070
hay	8.90	11.18	0.020	0.090
straw	26.74	7.94	0.030	0.280
grain	0.08	4.97	0.008	< 0.01

A comparison of metabolites detected in wheat after spray application (phenyl- and triazole-label) and seed treatment (phenyl-label, 5× overdose experiment) of wheat with prothioconazole is given in Table 13.

Table 13 Comparison of metabolites detected in wheat forage and hay after spray application (phenyl- and triazole-label) and seed treatment (phenyl-label, 5× overdose experiment) of prothioconazole in percent of TRR

Compound	Forage			Hay		
treatment	foliar		seed	foliar		seed
label	phenyl	triazole	phenyl	phenyl	triazole	phenyl
TRR in mg ai. eq/kg	*10.45*	*7.957*	*0.070*	*8.90*	*11.174*	*0.090*
Prothioconazole	3.3	5	0.4	2.6	3	0.8
Metabolites common to both labels:						
M02	7.1		0.6	3.3		0.2
M59 + M63					1	
M59 + M21-23		1				
M59 + M54-56					*1*	
M03	6.9	2	1.3	5.1	n.d.[a]	
M11	2.5		2.1	0.9		1.5
M04	35.4	19	10.9	18.5	11	6.4
M63		1				
M14	2.4	2[b]	12.0[b]	8.5	n.d[a]	3.8
M15	1.2			6.7		
M17	1.1		1.5	1.2		1.8
M14-17	0.1			0.5		
M21-23	8.6	1		2.6	1	
M21-23 + M54-56		1			3	
M54-56		1			3	
(sum of phenyl-hydroxylated compounds of M04)	*(13.4)*	*(6[c])*	*(13.5)*	*(19.5)*	*(8[d])*	*(5.6)*
M18	4.5	9	1.5	9.4	7	2.5
M19		3		4.6	n.d.[a]	0.2
M65		2				
M44		2				
Metabolite specific to the phenyl-label:						
M43				0.7		0.8
Metabolites specific to the triazole-label:						
M31		12			25	
M30		3			8	
M30/M29		< 1			2	
M29		1			5	
M46		1			2	

Compound	Forage			Hay		
treatment	foliar		seed	foliar		seed
label	phenyl	triazole	phenyl	phenyl	triazole	phenyl
Metabolites identified as group:						
ai, M03, M04, M18, M29; M30, M31					2	
Total identified	73.1	66	30.3	64.7	75	18.0
Additional characterised	12.3	28	7.0	22.3	21	1.4
Total radioactive residue (TRR)	100	100	100	100	99	100

M02 = JAU 6476-sulfonic acid
M03 = JAU 6476-triazolinone
M04 = JAU 6476-desthio
M11 = JAU 6476-disulfide
M14 = JAU 6476-desthio-3-hydroxy
M15 = JAU 6476-desthio-4-hydroxy
M16 = JAU 6476-desthio-5-hydroxy
M17 = JAU 6476-desthio-6-hydroxy
M18 = JAU 6476-desthio-α-hydroxy
M19 = JAU 6476-desthio-α-acetoxy
M21 =JAU 6476-desthio-3-hydroxy-glucoside
M22 = JAU 6476-desthio-4-hydroxy-glucoside
M23 = JAU 6476-desthio-6-hydroxy-glucoside
M29 = triazolylacetic acid = TAA
M30 = triazolylhydroxypropionic acid = THP
M31 = triazolylalanine = TA
M43 = JAU 6476-benzylpropyldiol-glucoside
M44 = JAU 6476-desthio-phenyl-cysteine
M46 = JAU 6476-triazolyl-ethanol-glucoside
M54 = JAU 6476-desthio-3-hydroxy-glucoside-malonic acid
M55 = JAU 6476-desthio-4-hydroxy-glucoside-malonic acid
M56 = JAU 6476-desthio-6-hydroxy-glucoside-malonic acid
M59 = JAU 6476-hydroxy-sulfonic acid glucoside
M63 = JAU 6476-desthio-glucoside-malonic acid
M65 = JAU 6476-desthio-dihydroxy-glucoside-malonic acid

[a] not determined, metabolite was seen during isolation and identification

[b] sum of M14 and M15

[c] including fraction M21-23 and M59

[d] including fraction of M54-56 and M59

Table 14 Comparison of metabolites detected in wheat straw and grain after spray application (phenyl- and triazole-label) and seed treatment (phenyl-label, 5× overdose experiment) of prothioconazole in percent of TRR

Compound	Straw			Grain		
treatment	foliar		seed	foliar		seed
label	phenyl	triazole	phenyl	phenyl	triazole	phenyl
TRR in mg ai equivalents/kg	*26.74*	*7.942*	*0.280*	*0.0800*	*4.972*	[a]
Prothioconazole	3.7	6	0.6	1.0		[a]
Metabolites common to both labels:						
M02	8.4		0.4			[a]
M03	6.1	1		1.3		
M11	1.3			1.3		
M04	22.3	9	6.6	15.9		
M14	2.9		3.8	1.1[b]		
M15	2.7		2.4			
M17	1.2		2.9			
M14-17	0.7	7				
M21-23	7.3	1	10.6	8.4		
M54-56		4				
(sum of phenyl-hydroxylated compounds of M04)	*(14.8)*	*(12)*	*(19.7)*	*(9.5)*		
M18	5.8	7	3.3	2.8		

Compound	Straw			Grain		
treatment	foliar		seed	foliar		seed
label	phenyl	triazole	phenyl	phenyl	triazole	phenyl
M19		2	0.8	0.4		
Metabolites specific to the phenyl-label:						
M09 / M19	2.0					[a]
M43	1.8		1.4	1.5		
Metabolites specific to the triazole-label:						
M31		4			71	[a]
M30		8			< 1	
M30/M29		1				
M29		5			19	
M45		2				
M46		2				
Metabolites identified as group:						
ai, M03, M04, M18, M29; M30, M31		2				
Total identified	66.2	61	32.8	33.7	94	[a]
Additional characterised	19.0	35	47.5	36.8	6	[a]
Total radioactive residue (TRR)	100	100	100	100	100	[a]

M21 = JAU 6476-desthio-3-hydroxy-glucoside,

M45 = JAU 6476-triazolyl-ethanol,

For codes of metabolites see Table 13,

[a] TRR below threshold value of 0.01 mg/kg

[b] sum of M14 and M15

The metabolism of JAU 6476-desthio (M04) was investigated to determine its overall metabolic fate and the total radioactive residues in summer wheat following spray application (Vogeler, K; Sakamoto, H and Brauner, A, 1993). The test substance, formulated as WP25, was applied twice, first at growth stage of one node (BBCH 31) and 27 days later (end of heading, BBCH 59) at a rate of approximately 250 g JAU 6476-desthio/ha. The summer wheat plants were grown under environmental conditions (sunlight and temperatures). A glass roof protected the plants from rainfall. The soil was surface irrigated.

Forage samples were collected immediately (day 0) and 14 days after the second application. Mature wheat samples (straw, glumes and grain) were harvested 48 days after the second application

The test compound JAU 6476-desthio was slowly metabolised in wheat. The percentages of TRR and mg eq/kg JAU 6476-desthio of the metabolites identified are summarised in the Table 15.

Table 15 JAU 6476-desthio and its metabolites after spray application of triazole-labelled JAU 6476-desthio to wheat (in percent of TRR and mg ai eq/kg)

Compound	Forage (day 0)		Forage (day 14)		Straw		Grain	
	% of TRR	mg/kg	% of TRR	mg/kg	% of TRR	mg/kg	% of TRR	mg/kg
JAU 6476-desthio *(M04)*	86.8	8.94	76.9	8.36	71.9	20.61	2.3	0.07
JAU 6476-desthio-3-hydroxy *(M14)*	1.2	0.12	1.5	0.16	1.3	0.37		
JAU 6476-desthio-4-hydroxy *(M15)*	0.8	0.08	1.8	0.20	0.8	0.23		
JAU 6476-desthio-5-hydroxy *(M16)*	1.5	0.15	1.8	0.20	0.8	0.23		
JAU 6476-desthio-6-hydroxy *(M17)*	0.3	0.03	0.5	0.06	0.2	0.06		
JAU 6476-desthio-α-hydroxy *(M18)*	1.6	0.16	3.5	0.37	4.3	1.23	0.1	< 0.01

Compound	Forage (day 0)		Forage (day 14)		Straw		Grain	
	% of TRR	mg/kg	% of TRR	mg/kg	% of TRR	mg/kg	% of TRR	mg/kg
TA *(M31)*	0.3	0.03	1.3	0.14	0.2	0.06	60.2	1.72
THP *(M30)*	0.6	0.06	1.4	0.16	3.2	0.92		
TAA *(M29)*	0.6	0.06	1.2	0.13	0.9	0.26	31.9	0.91
Total identified	93.7	9.63	89.9	9.78	83.6	23.99	94.5	2.69
Additional characterised	4.4	0.47	6.9	0.74	9.1	2.59		
Solids	1.5	0.15	2.5	0.27	6.8	1.95	0.6	0.02
Total radioactive residue (TRR)		10.29		10.87		28.67		2.85

Peanuts

The behaviour and metabolism of prothioconazole after spray application to peanuts was investigated using phenyl (Haas, M, 2001) and triazole-labelled (Haas, M, 2003) parent compound. In both trials peanuts were treated three times at growth stages from pegging to beginning of pod development (Growth stage 66–75 according to BBCH) allowing a three week time period between the three applications and a 14 day interval until harvest (PHI). Each treatment was performed using radio-labelled prothioconazole formulated as an EC 250 and at a rate of 297 g ai/ha. This approximates the maximum annual field rate recommended for peanuts in the United States.

A 5× application was also tested in order to collect sufficient amounts of radioactivity for identifying metabolites. For this experiment, formulated phenyl-labelled prothioconazole was applied with a hand sprayer. The treated plants were placed in a greenhouse with a day/night rhythm of 14/10 hours at an average temperature of 20-24 °C (day) and 16–17 °C (night) and at a relative humidity of 60%.

Peanut plants were removed from soil at maturity at BBCH growth stages 89–91, 14 days after the third application. Nuts were cut off the plants and cleaned from sticking soil. Plants and nuts were allowed to dry for 4–5 days.

The mg ai eq/kg and the percentages of the TRR of prothioconazole and its metabolites after the use of phenyl- and triazole-labelled prothioconazole in peanuts are given in Table 16 and Table 17, respectively.

Table 16 Parent compound and metabolites after spray application of phenyl and triazole-labelled prothioconazole to peanuts (mg ai. eq/kg)

	Hay		Nutmeat		
Label	phenyl	triazole	phenyl		triazole
Parent compound / metabolite			extraction 2[a]	extraction 1[b]	
Prothioconazole	1.98	3.11			
Metabolites common to both labels:					
M02	2.28	1.26		< 0.01	
M03	1.72	1.66			
M11	3.48	2.55			
Σ: M25, M26	7.89	0.72			
M04	30.37	11.15			0.09
M14	7.81	3.13			
M15	2.19	1.40			
M14 or M15[c]	0.31				
Σ: M21, M22	0.97	3.62	< 0.01	< 0.01	

	Hay		Nutmeat		
Label	phenyl	triazole	phenyl		triazole
Parent compound / metabolite			extraction 2[a]	extraction 1[b]	
Prothioconazole	1.98	3.11			
Σ: M54, M55		2.82			
M24	5.59		0.03	0.02	
Σ: M47, M64		2.00			
M64	15.09		0.02	0.04	
M44		0.78			
Metabolites specific to the triazole-label:					
M31		0.56			0.67
M30		0.30			0.34
M29		0.33			0.02
M45		0.26			
M46		0.71			
Σ: fatty acids			0.14	0.13	0.04
Total identified	79.68	36.36	0.20	0.20	1.16
Total radioactive residue (TRR) mg/kg	107.51	47.38	0.29	0.30	1.40

ai = prothioconazole	M26 = JAU 6476-dihydroxy-olefin-sulfonic acid
M02 = JAU 6476-sulfonic acid	M29 = triazolylacetic acid (TAA)
M03 = JAU 6476-triazolinone	M30 = triazolylhydroxypropionic acid (THP)
M04 = JAU 6476-desthio	M31 = triazolylalanine (TA)
M11 = JAU 6476-disulfide	M44 = JAU 6476-desthio-phenyl-cysteine
M14 = JAU 6476-desthio-3-hydroxy	M45 = JAU 6476-triazolyl-ethanol
M15 = JAU 6476-desthio-4-hydroxy	M46 = JAU 6476-triazolyl-ethanol-glucoside
M21 = JAU 6476-desthio-3-hydroxy-glucoside	M47 = JAU 6476-desthio-dihydroxy-diene-glucoside
M22 = JAU 6476-desthio-4-hydroxy-glucoside	M54 = JAU 6476-desthio-3-hydroxy-glucoside-malonic acid
M24 = JAU 6476-desthio-hydroxy-dienyl-cysteine	M55 = JAU 6476-desthio-4-hydroxy-glucoside-malonic acid
M25 = JAU 6476-dihydroxy-diene-sulfonic acid	M64 = JAU 6476-desthio-dihydroxy-olefin-glucoside

[a] extraction procedure 2 (MSPD

[b] extraction procedure 2 (n-hexane reflux)

[c] trace amounts, no discrimination between isomers possible

Table 17 The proportion of parent compound and metabolites after spray application of phenyl and triazole-labelled prothioconazole to peanuts (in percent of TRR)

	Hay		Nutmeat		
Label	phenyl	triazole	phenyl		triazole
Parent compound / metabolite			extraction 2	extraction 1	
TRR in mg ai eq/kg	107.51	47.38	0.29	0.30	1.40
Prothioconazole	1.8	6.6			1.3
Metabolites common to both labels:					
M02	2.1	2.7		1.5	
M03	1.6	3.6			
M11	3.2	5.4			

	Hay		Nutmeat		
Label	phenyl	triazole	phenyl		triazole
Parent compound / metabolite			extraction 2	extraction 1	
Σ: M25, M26	7.4	1.5			
M04	28.2	23.6			6.2
M14	7.3	6.6			
M15	2.0	3.0			
M14 or M15[c]	0.3				
Σ: M21, M22	0.9	7.6	1.0	3.4	
Σ: M54, M55		6.0			
M24	5.2		9.0	5.4	
Σ: M47, M64		4.2			
M64	14.1		7.6	12.2	
M44		1.7			
Metabolites specific to the triazole-label:					
M31		1.2			47.8
M30		0.6			24.5
M29		0.7			1.2
M45		0.5			
M46		1.5			
Σ: fatty acids			47.8	42.6	3.0
Total identified	74.1	77.0	65.4	65.1	82.7
Total radioactive residue (TRR)	100.0	100.0	100.0	100.0	100.0
Description of the metabolites identified is given under Table 16					

Sugar beets

The behaviour and metabolism of prothioconazole after spray application to sugar beets was investigated using phenyl (Beedle, EC and Ying, SL, 2004) and triazole-labelled (Beedle, EC and Ying, SL, 2004a) parent compound.

Four foliar spray applications of prothioconazole were made to sugar beet plants at an average rate of 288 and 289 g ai/ha/application for a total rate of 1152 and 1157 g ai/ha of the phenyl or triazole-labelled parent compound, respectively. Applications were made at 14-day intervals with the last application occurring at seven days prior to harvest of sugar beet tops and sugar beet roots. The sugar beet plants were moved to a fenced area outside of the greenhouse and remained there until harvest.

Sugar beet tops and roots were harvested 149 days after planting. The tops from the plants were cut from the roots at the point of attachment, combined, weighed, and placed in a freezer. The roots were dug from the soil, rinsed gently with water to remove dirt, combined, dried, weighed, cut into smaller pieces, and placed also in the freezer.

The total radioactive residues (TRRs) in sugar beet tops and roots were determined by combustion and radioassay of unextracted samples and were expressed as mg ai eq/kg. The final extracts were analysed using different HPLC-systems within 28 days of extraction. Identification was performed by HPLC-MS/MS after isolation of the metabolites by preparative HPLC. Some minor metabolites were identified by HPLC comparison only.

The mg ai eq/kg and the percentages of the TRR of prothioconazole and its metabolites after the use of phenyl- and triazole-labelled prothioconazole are given in Tables 18 and 19, respectively.

Table 18 The concentration of parent compound and metabolites after spray application of phenyl- and triazole-labelled prothioconazole to sugar beets (mg ai eq/kg)

Parent compound / metabolite	Sugar beet tops		Sugar beet roots	
label	phenyl	triazole	phenyl	triazole
Prothioconazole	0.323	0.265		
Metabolites common to both labels:				
M02		0.205		
M59	0.351	0.316		
M60	0.083			
M03	0.088	0.105	0.003	0.002
M04	1.249	0.988	0.068	0.033
M14/M15/M16/M17		0.063		
M21/M22/M23	0.222	0.334		
M18	0.069			
M24	0.454	0.512		0.007
Metabolites specific to the triazole-label:				
M30		0.207		
M31		0.084		0.038
M45		0.194		
M46 and M62		0.263		
Total identified	2.839	3.536	0.071	0.080
Additional characterised	1.437	1.519	0.038	0.042
Solids	0.056	0.099	0.010	0.008
Total radioactive residue (TRR)	4.333	5.154	0.119	0.130

ai = prothioconazole	M22 = JAU 6476-desthio-4-hydroxy-glucoside
M02 = JAU 6476-sulfonic acid	M23 = JAU 6476-desthio-6-hydroxy-glucoside
M03 = JAU 6476-triazolinone	M24 = JAU 6476-desthio-hydroxy-dienyl-cysteine
M04 = JAU 6476-desthio	M30 = triazolylhydroxypropionic acid (THP)
M14 = JAU 6476-desthio-3-hydroxy	M31 = triazolylalanine (TA)
M15 = JAU 6476-desthio-4-hydroxy	M45 = JAU 6476-triazolyl-ethanol
M16 = JAU 6476-desthio-5-hydroxy	M46 = JAU 6476-triazolyl-ethanol-glucoside
M17 = JAU 6476-desthio-6-hydroxy	M59 = JAU 6476-hydroxy-sulfonic acid glucoside
M18 = JAU 6476-desthio-α-hydroxy	M60 = JAU 6476-hydroxy-disulfonic acid glucoside
M21 = JAU 6476-desthio-3-hydroxy-glucoside	M62 = JAU 6476-triazolyl-sulfonic acid-ethanol-glucoside

Table 19 Parent compound and metabolites after spray application of phenyl- and triazole-labelled prothioconazole to sugar beets (in percent of TRR)

Parent compound / metabolite	Sugar beet tops		Sugar beet roots	
label	phenyl	triazole	phenyl	triazole
TRR in mg ai equivalents/kg	4.333	5.154	0.119	0.130
Prothioconazole	7	5		
Metabolites common to both labels:				
M02		4		
M59	8	6		
M60	2			

Parent compound / metabolite	Sugar beet tops		Sugar beet roots	
label	phenyl	triazole	phenyl	triazole
M03	3	2	2	2
M04	28	19	58	25
M14/M15/M16/M17		1		
M21/M22/M23	5	6		
M18	2			
M24	10	10		5
Metabolites specific to the triazole-label:				
M30		4		
M31		2		29
M45		4		
M46 and M62		5		
Total identified	65	69	60	61
Additional characterised	33	29	32	33
Solids	1	2	8	6
Total radioactive residue (TRR)	100	100	100	100

Description of the metabolites identified is given under Table 18

Environmental fate in soil

The Meeting received information on the fate and behaviour of prothioconazole in the environment. In the studies phenyl and triazole-labelled as well as the non-labelled parent compound was used. In addition, studies with the metabolites JAU 6476-S-methy (M01) and JAU 6476-desthio *(*M04)-phenyl-labelled and non-labelled were provided.

Aerobic degradation of prothioconazole was studied in a sandy loam and silty clay loam soils (Gilges, M, 2000) at a rate of 600 g/ha/15 cm soil depth corresponding to the maximum field rate of 200 g/ha/single treatment. The characteristics of the soils are given in Table 20.

Table 20 Soils used to investigate degradation of JAU 6476-S-methyl *(M01)* under aerobic conditions

Origin	Höfchen Rhineland Germany	Laacher Hof AIII Rhineland Germany	Laacher Hof AXXa Rhineland Germany	Stanley Kansas USA
Soil classification (DIN)	1.loamy silt	2. loamy silt	sandy loam	silty clay
Textural analysis (USDA):				
2000–50 µm, sand (%)	8.5	36.9	72.4	2.6
50–2 µm, silt (%)	81.3	51.1	22.6	56.4
< 2 µm, clay (%)	10.2	12.0	5.0	41.0
pH values:				
in water	7.3	7.9	7.2	6.3
in $CaCl_2$	6.5	6.7	6.3	5.2
Organic C (%)	1.55	0.98	1.02	1.46
Organic matter (%) [factor: 1.72]	2.67	1.69	1.75	2.51
Cation exchange capacity (meq/100 g)	15	8	8	24
Particle density (g/cm³)	2.09	2.55	2.5	2.47
Max. water holding capacity (g/100 g DM)	63.1	36.4	34.4	43.8

The soil moisture was adjusted to 48%, and the soil batches were incubated under aerobic conditions in the dark at 20 °C for a testing period of 120 days. Determinations of the microbial biomass were carried out at the beginning and at the end of the test. Samples were taken for analysis at day 0, 1, 3, 7, 14, 30, 63, 90 and 120 post-treatment.

Soils were extracted immediately after sampling by shaking with acetonitrile/water (80/20). The radioactivity was determined in all samples and the extracts were analysed by TLC and HPLC methods. Prothioconazole and its degradation products had been identified by co-chromatography with reference standards using three TLC methods. Volatile radioactivity was trapped using polyurethane plugs and soda lime. The radioactivity (i.e., $^{14}CO_2$) absorbed by the soda lime was liberated with HCl.

The recovered radioactivity is summarised in Table 21.

Table 21 Radioactivity balance of prothioconazole after application to loamy silt (Laacher Hof) and silty clay (Stanley) soil (in percentage of the applied radioactivity)

Soil	Days after appl.	Soil			Volatiles		Material balance
		Extracted [a]	Bound [b]	Total soil	$^{14}CO_2$	Other volatiles	
Sandy Loam	0	89.0	10.7	99.7	n.m.	n.m.	99.7
	1	62.0	28.6	90.6	0.4	< 0.1	90.9
	3	62.3	31.2	93.4	1.0	< 0.1	94.5
	7	61.6	33.6	95.2	2.4	< 0.1	97.6
	14	55.4	40.5	95.9	2.7	< 0.1	98.6
	30	52.8	40.5	93.3	3.7	< 0.1	97.0
	63	52.8	40.3	93.3	5.4	< 0.1	98.6
	90	51.0	39.6	90.6	5.9	< 0.1	96.5
	120	57.3	35.6	92.9	4.1	< 0.1	97.0
Silty clay loam	0	86.6	10.9	97.6	n.m.	n.m.	97.6
	1	64.6	30.7	95.3	< 0.1	< 0.1	95.3
	3	52.8	39.5	92.3	0.1	< 0.1	92.4
	7	51.8	43.2	95.0	0.6	< 0.1	95.5
	14	47.2	44.8	92.0	1.9	< 0.1	93.9
	30	51.0	39.4	90.4	3.8	< 0.1	94.2
	63	48.3	42.7	91.0	4.9	< 0.1	96.0
	90	46.3	43.3	89.6	5.3	< 0.1	94.9
	120	44.9	46.2	91.1	5.5	< 0.1	96.6

[a] extracted: organic cold extract + organic hot extract

[b] not extracted: soil + filter

The metabolic pathway of degradation of prothioconazole is shown in Figure 3.

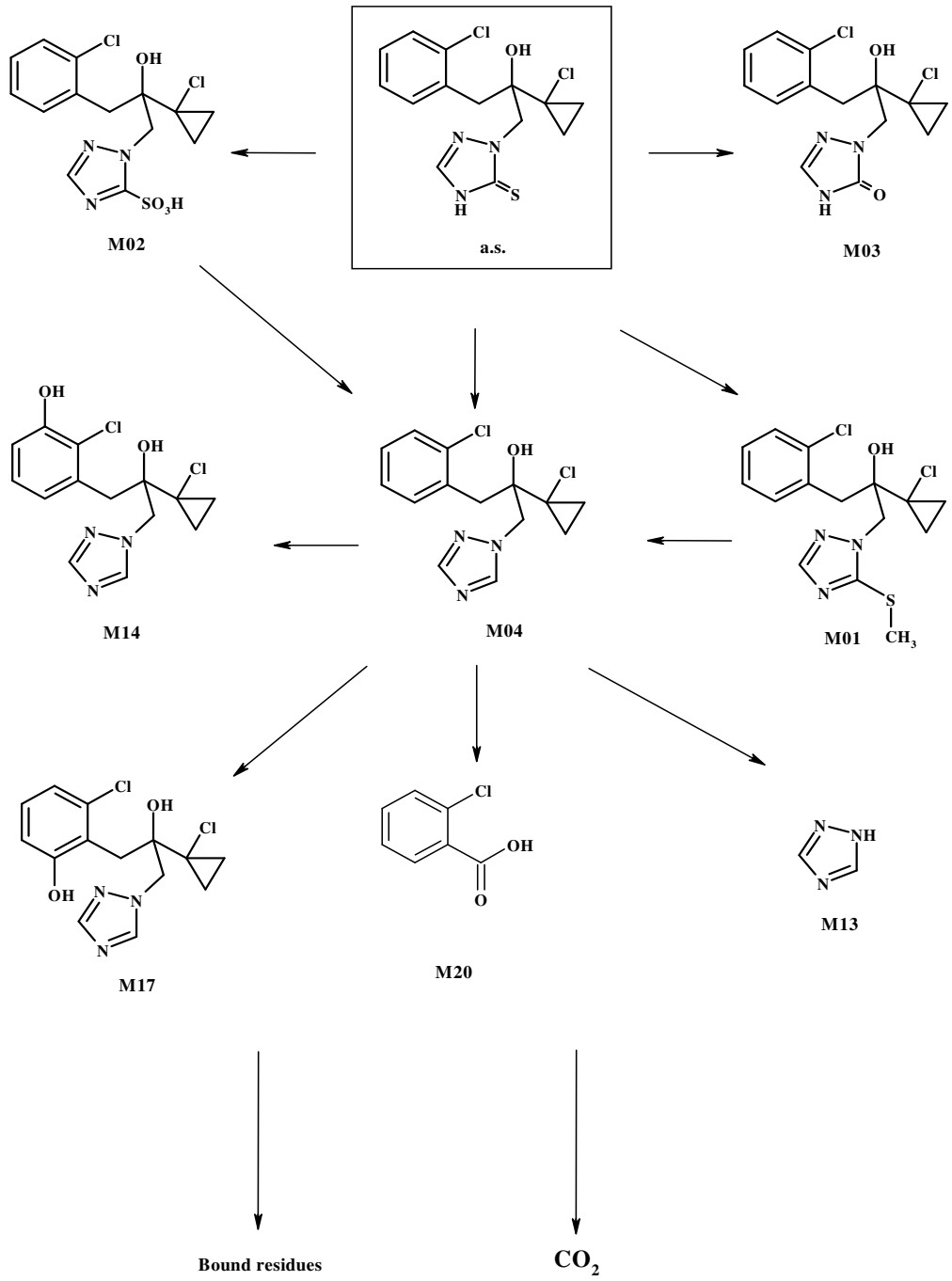


Figure 3 Proposed metabolic pathway of prothioconazole in soil

as	= prothioconazole	M13	= 1,2,4-triazole
M01	= JAU 6476-S-methyl	M14	= JAU 6476-desthio-3-hydroxy
M02	= JAU 6476-sulfonic acid	M17	= JAU 6476-desthio-6-hydroxy
M03	= JAU 6476-triazolinone	M20	= 2-chlorobenzoic acid
M04	= JAU 6476-desthio		

The distribution of the active ingredient and the degradation products are summarised in Table 22.

Table 22 Distribution of the active ingredient and degradation products after application of prothioconazole to two soils and incubation at 20 °C under aerobic conditions (in percent of the applied radioactivity)

Soil	Days after appl.	ai	M01	M02	M03	M04	M14/M15/M16	Other [a]
Sandy loam	0	82.1	< 0.1	n.d.	< 0.1	4.1	n.d.	2.8
	1	15.2	3.8	n.d.	< 0.1	38.6	n.d.	4.3
	3	10.6	3.2	1.2	1.2	41.3	1.1	3.7
	7	7.7	2.9	2.1	1.3	39.0	3.2	5.4
	14	5.2	2.4	1.2	1.1	36.0	2.7	6.9
	30	4.4	2.2	3.2	0.7	35.5	2.1	4.6
	63	2.5	1.9	3.1	1.8	36.6	2.0	5.0
	90	2.4	1.9	3.0	2.0	35.3	2.1	4.4
	120	3.1	1.7	3.0	1.7	42.3	1.4	4.2
Silt clay loam	0	81.9	0.2	0.1	0.1	2.8	n.d.	1.6
	1	38.8	3.4	n.d.	0.5	15.0	n.d.	7.0
	3	23.2	5.2	n.d.	0.7	19.2	n.d.	4.5
	7	15.5	5.5	1.3	1.1	20.9	1.3	6.2
	14	11.7	4.0	2.2	1.1	18.7	1.8	7.8
	30	12.6	3.3	3.1	2.9	19.7	2.9	6.5
	63	10.3	2.2	3.7	3.1	19.9	2.6	6.4
	90	9.6	1.7	4.0	2.7	19.9	2.6	5.8
	120	10.5	1.5	3.8	2.4	18.5	2.2	6.0

ai = prothioconazole	M01 = JAU 6476-S-methyl
M02= JAU 6476-sulfonic acid	M03 = JAU 6476-triazolinone
M04 = JAU 6476-desthio	M14/M15/M16 = mixture of JAU 6476-desthio-3-hydroxy, JAU 6476-desthio-4-hydroxy and JAU 6476-desthio-5-hydroxy

n.d. not detected

[a] origin + minor metabolites + diffuse radioactivity

The aerobic degradation and metabolism of prothioconazole was studied in silt loam and loamy sand soils (Hellpointner, E; 2001a) for a maximum of 365 days under aerobic conditions in the dark at 20 °C, using the phenyl and the triazole-radiolabelled active substance applied at a rate of 0.26 mg ai/kg soil corresponding to the maximum field rate of 600 g/ha/15 cm soil. The soil moisture was adjusted to 50% water-holding capacity of the silt loam soil and 75% of 1/3 bar moisture for the loamy sand soil.

The test system was investigated at day 0, 1, 2, 3, 7, 14, 30, 63, 90, 120, 181, 272 and 365.

The 100 g soil samples were extracted three times at room temperature with acetonitrile/water (80:20, v:v) stabilised by addition of cysteine-hydrochloride. The prothioconazole residues were analysed by normal phase radio-thin-layer chromatography. For identification of the transformation products co-chromatography, LC/MS and LC/MS/MS methods were used.

During the study the total mean recovery of the applied radioactivity in individual test vessels was 96 and 96.3% for the two soils. The complete material balance found at all sampling intervals demonstrated that no significant radioactivity dissipated from the vessels or was lost during processing.

The results for the distribution of the active substance and the degradation products are summarised in Table 23 and Table 24.

Table 23 Distribution of prothioconazole and its metabolites after application to the silt loam soil (in percent of applied radioactivity)

Label	Days after appl.	ai	M01[a]	M02[a]	M03[a]	M04[a]	M13[b]	M14[b]	M17[b]	M20[b]	Unknown metabolites[c,d]
Phenyl	0	73.4	< 2.0	n.d.	n.d.	15.9		n.d.	n.d.	n.d.	< 2.0
	1	7.9	11.3	n.d.	n.d.	39.8		< 2.0	< 2.0	n.d.	2.2
	3	6.1	10.7	n.d.	< 2.0	38.6		< 2.0	< 2.0	n.d.	2.3
	7	2.0	10.3	n.d.	n.d.	46.5		< 2.0	< 2.0	n.d.	< 2.0
	14	4.2	8.4	n.d.	n.d.	35.8		< 2.0	3.1	n.d.	2.7
	30	2.9	7.5	n.d.	< 2.0	35.2		< 2.0	3.4	n.d.	2.9
	63	2.2	6.4	n.d.	n.d.	35.0		< 2.0	3.2	n.d.	2.5
	90	< 2.0	6.6	< 2.0	n.d.	33.8		n.d.	2.2	n.d.	< 2.0
	120	< 2.0	6.0	3.2	< 2.0	17.5		< 2.0	4.2	< 2.0	n.d.
	181	< 2.0	4.9	3.7	n.d.	16.8		n.d.	2.0	n.d.	n.d.
	272	< 2.0	2.6	3.1	< 2.0	8.8		< 2.0	2.9	< 2.0	< 2.0
	365	< 2.0	2.8	3.1	< 2.0	6.3		< 2.0	2.9	< 2.0	< 2.0
Triazole	0	81.0	< 2.0	n.d.	n.d.	10.2	n.d.	n.d.	n.d.	n.d.	< 2.0
	1	9.0	12.8	n.d.	n.d.	38.8	n.d.	< 2.0	< 2.0	n.d.	< 2.0
	3	6.7	11.8	n.d.	< 2.0	39.4	n.d.	< 2.0	< 2.0	n.d.	2.5
	7	< 2.0	10.7	n.d.	n.d.	49.4	n.d.	n.d.	< 2.0	n.d.	< 2.0
	14	4.6	10.3	n.d.	n.d.	39.5	n.d.	2.1	2.4	n.d.	2.7
	30	3.1	9.0	< 2.0	< 2.0	37.7	n.d.	< 2.0	3.3	n.d.	3.0
	63	< 2.0	7.4	< 2.0	n.d.	35.9	n.d.	< 2.0	3.3	n.d.	3.3
	90	< 2.0	6.3	2.4	n.d.	34.8	n.d.	n.d.	2.1	n.d.	3.0
	120	5.6	6.4	3.3	< 2.0	15.1	< 2.0	< 2.0	4.6	< 2.0	n.d.
	181	< 2.0	5.2	8.3	n.d.	16.6	n.d.	n.d.	2.4	n.d.	< 2.0
	272	6.6	3.1	3.5	n.d.	7.9	< 2.0	< 2.0	2.6	2.2	< 2.0
	365	5.9	3.1	3.3	< 2.0	6.1	n.d.	n.d.	2.3	< 2.0	< 2.0

ai = prothioconazole

M01 = JAU 6476-S-methyl

M02 = JAU 6476-sulfonic acid
M03 = JAU 6476-triazolinone
M04 = JAU 6476-desthio
M13 = 1,2,4-triazole

M14 = JAU 6476-desthio-3-hydroxy

M17 = JAU 6476-desthio-6-hydroxy

M20 = 2-chlorobenzoic acid

[a] = identified

[b] = characterised

[c] = phenyl-label: sum of three unknown metabolites, none did exceed 3% of the applied radioactivity

[d] =triazole-label: sum of three unknown metabolites, none did exceed 3.5% of the applied radioactivity

n.d. = not detected

Table 24 Distribution of prothioconazole and its metabolites after application to the loamy sand soil (in percent of applied radioactivity)

Label	Days after appl.	ai	M01[a]	M02[a]	M03[a]	M04[a]	M13[b]	M14[b]	M17[b]	M20[b]	Unknown metabolites [c]
Phenyl	0	89.9	< 2.0	n.d.	n.d.	7.5		n.d.	n.d.	n.d.	n.d.
	1	46.3	6.6	n.d.	n.d.	14.3		n.d.	n.d.	n.d.	< 2.0
	3	20.5	11.3	n.d.	< 2.0	21.0		n.d.	n.d.	n.d.	< 2.0
	7	8.5	13.7	n.d.	n.d.	31.7		n.d.	n.d.	n.d.	< 2.0
	14	8.2	12.9	n.d.	< 2.0	28.8		n.d.	n.d.	n.d.	< 2.0
	30	5.2	12.3	n.d.	< 2.0	28.3		n.d.	n.d.	n.d.	< 2.0
	63	4.3	11.7	n.d.	< 2.0	32.6		n.d.	n.d.	n.d.	< 2.0
	90	4.8	8.3	n.d.	< 2.0	41.2		n.d.	n.d.	n.d.	< 2.0
	120	2.5	9.8	< 2.0	< 2.0	23.9		< 2.0	< 2.0	< 2.0	< 2.0
	181	2.4	9.2	< 2.0	< 2.0	29.5		n.d.	< 2.0	n.d.	< 2.0
	272	4.1	7.0	< 2.0	< 2.0	23.5		< 2.0	< 2.0	< 2.0	< 2.0
	365	2.3	7.1	< 2.0	< 2.0	21.9		< 2.0	< 2.0	< 2.0	< 2.0
Triazole	0	95.5	n.d.	n.d.	n.d.	2.4	n.d.	n.d.	n.d.	n.d.	n.d.
	1	52.1	6.4	n.d.	n.d.	11.7	n.d.	n.d.	n.d.	n.d.	< 2.0
	3	24.6	12.4	n.d.	< 2.0	20.9	n.d.	n.d.	n.d.	n.d.	< 2.0
	7	8.4	14.6	n.d.	< 2.0	31.7	n.d.	n.d.	n.d.	n.d.	< 2.0
	14	9.2	14.4	n.d.	< 2.0	29.9	n.d.	n.d.	n.d.	n.d.	< 2.0
	30	5.1	13.2	n.d.	< 2.0	30.0	n.d.	n.d.	n.d.	n.d.	< 2.0
	63	3.4	13.2	n.d.	< 2.0	34.0	n.d.	n.d.	n.d.	n.d.	< 2.0
	90	2.6	11.7	n.d.	< 2.0	38.4	n.d.	n.d.	n.d.	n.d.	< 2.0
	120	2.1	10.8	< 2.0	< 2.0	25.1	< 2.0	< 2.0	< 2.0	< 2.0	< 2.0
	181	2.3	10.2	< 2.0	< 2.0	29.1	n.d.	n.d.	< 2.0	n.d.	< 2.0
	272	3.8	7.2	2.0	< 2.0	23.2	n.d.	< 2.0	< 2.0	< 2.0	< 2.0
	365	4.6	7.6	2.3	< 2.0	23.7	< 2.0	< 2.0	< 2.0	< 2.0	< 2.0

Description of the metabolites identified is given under Table 23

[a] identified

[b] characterised

[c] sum of two unknown metabolites, both < 2% of the applied radioactivity

n.d. = not detected

Degradation of JAU6476-S-methyl (M01, one of the major soil metabolites) was studied in four soils (two loamy silts, sandy loam and silty clay) under aerobic conditions (Gilges, M; 2001). The application rate of phenyl-labelled JAU 6476-S-methyl (M01) (30 g/ha) corresponded to the maximum level of the M01 observed after application of the parent compound at maximum recommended rate of 200g as/ha/application. The soil samples were incubated in the dark at 20 °C for 125 days at a moisture content of 40% of the maximum water holding capacity. The total recoveries of day 0 were taken as 100% of applied radioactivity for calculation of material balance.

The sampling dates were day 0 in duplicate (after about 2 h), 1, 3, 7, 14, 30, 59, 90 and 125 days after treatment. The characteristics of the soils are summarised in Table 20.

The total recoveries of the applied radioactivity ranged from 90 to 99% in soil Höfchen, from 96 to 105% in soil (Laacher Hof AIII), from 90 to 102% in soil (Laacher Hof AXXa), and from 92 to 117% in soil (Stanley) during the test period of 125 days. The amount of radioactivity bound to soil

increased during the test period and reached a maximum of 35% at day 59 and decreased at the end of the test period to 31% (soil Höfchen). The amount of radioactivity bound to soil (Laacher Hof AIII) reached a maximum of 43% at day 125. The amount of radioactivity bound to soil (Laacher Hof AXXa) reached a maximum of 39% at the end of the test. The amount of radioactivity bound to soil Stanley reached the maximum also at day 125 (35%) (values expressed in percent of applied radioactivity). Due to the increase of the amount of bound residues and due to high mineralisation the amounts of radioactivity which could be extracted decreased with time and accounted for 7.5% (Höfchen), 34.2% (Laacher Hof AIII), 14% (Laacher Hof AXXa) and for 77% (Stanley) after 125 days.

In soil JAU 6476-S-methyl *(M01)* was degradable under aerobic conditions. The test substance was thoroughly metabolised to carbon dioxide in all four soils tested with a maximum of 54% (soil Höfchen). After 125 days of incubation two metabolites were detected in silt clay soil with maximum levels of 27% and 11% of the applied radioactivity. No further metabolites were present at levels higher than 10% at any sampling date of the study. These compounds were not characterised.

Degradation of JAU6476-desthio (M04, a major soil metabolite) was studied in four soils (two kinds of loamy silt, a sandy loam and a silty clay) under aerobic conditions in the dark (Giles M, 2001a). Phenyl-labelled JAU 6476-desthio (M04) was applied at 72.5 g/ha corresponding to the maximum level of the M04 observed after application of the parent compound at maximum recommended rate of 200 g as/ha/application. Soils were extracted immediately after sampling and the radioactivity determined in all samples and the extracts analysed by TLC in order to determine the concentration of the test substance and the degradation products as a function of the incubation time. The total recoveries of the applied radioactivity ranged from 91 to 103% during the test period of 120 days.

JAU 6476-desthio *(M04)* was degradable under aerobic conditions in soil. The test substance was thoroughly metabolised to carbon dioxide in all four soils tested with a maximum of 62%. Only a single metabolite above 5% of applied radioactivity was found which declined below 5% towards the end of the study. All further metabolites detected did not exceed 5% throughout the study.

The rate of degradation of prothioconazole in soil has been investigated in laboratory trials which were run with four different soil types under aerobic conditions at 20 °C. Additionally, laboratory trials (four different soils) with the two major metabolites (JAU 6476-S-methyl *(M01)* and JAU 6476-desthio *(M04)*) were performed. Furthermore, eight field trials were conducted at different sites in northern and southern Europe (Schramel, O; 2001) and USA (Wood, SE; 2004; Lenz, MF; 2004; Lenz, MF; 2004a).

The calculated DT_{50} values of prothioconazole determined in the laboratory soil degradation studies were in the range of 0.07 to 1.3 days (Gilges, M; 2000, amended 2001; Hellpointner, E; 2001). The DT_{50} values of the two major metabolites JAU 6476-S-methyl *(M01)* (Gilges, M; 2001) and JAU 6476-desthio *(M04)* (Gilges, M; 2001a) determined in the laboratory trials were in the range of 5.9 to 46 days and 7.0 to 34 days, respectively.

In the field, DT_{50} values for prothioconazole ranged from 1.3 to 2.8 days (mean: 1.7 days). The corresponding DT_{90} values were in the range of 4.4 to 9.3 days (mean: 5.8 days). The dissipation times for JAU 6476-desthio *(M04)* ranged from 16 to 72 days (mean: 42 days); the corresponding DT_{90} values ranged from 54 to 240 days (mean: 140 days). JAU 6476-S-methyl *(M01)* concentrations never exceeded the LOQ of 6 µg/kg, corresponding to less than 3% of the initial concentration of the active substance. No residues of prothioconazole or its metabolites were detected in a depth below 10 cm of soil, with the exception of the day 89 in one trial, where residues of JAU 6476-desthio *(M04)* were detected between the limit of detection and the LOQ in the 10–20 cm layer.

The DT_{50} and DT_{90} values obtained from the US trials are summarised in Table 25.

Table 25 Summary DT_{50} and DT_{90} values

Trial no.	Location	Prothioconazole		JAU 6476-desthio *(M04)*	
		DT_{50} (days)	DT_{90} (days)	DT_{50} (days)	DT_{90} (days)
110799	Byromville, Georgia, Canada	0.06[a]	-	37[b]	123[b]
200096	Minto, Manitoba, Canada	2.25[c]	7.48[c]	350[c]	-
200134	Saskatoon, Saskatchewan, Canada	2.04[c]	6.79[c]	410.8[c]	1364[c]

[a] Half-lives were determined using GraphPad Prism Software, using non-linear one phase exponential decay kinetics

[b] Half-lives were determined using GraphPad Prism Software, using linear regression and first order decay kinetics

[c] Half-lives were determined using GraphPad Prism Software (1st order decay kinetics)

The stability of residues in soil under deep-frozen conditions was tested in a silt loam soil (Sommer, H, 2002). The mean recoveries of prothioconazole, M01 and M04 were 945%, 101% and 102% in the concentration range of 6–200 µg/kg. The LOQ was 6 µg/kg. The results indicated that prothioconazole, JAU 6476-S-methyl *(M01)* and JAU 6476-desthio *(M04)* are stable in deep-frozen soil for at least 770 days. Degradation of prothioconazole could be observed only at room temperature, but no further degradation was seen under frozen conditions. However, prior to freezing and during extraction, losses of prothioconazole (bound residues, etc.) occurred. The results are shown in Table 26.

Table 26 Recovered amounts of prothioconazole and its metabolites in soil samples after storage under freezing conditions as percent of added amounts

Recovered amounts after storage for	Prothioconazole [a]	JAU 6476-S-methyl *(M01)*	JAU 6476-desthio *(M04)*
0 Days	35.5	102	101
770 Days	35.2	99.2	93.6
Relative difference (%)	–0.3	–2.8	–7.4

[a] For all storage stability samples, the time between spiking of the soil samples and deep freezing was about the same (3 h ± 30 min). Therefore, the day 0+3 h samples were used for prothioconazole in this table

In addition, all storage stability samples were analysed for the non-spiked substances in order to identify transformation processes. That means prothioconazole samples were also analysed for traces of JAU 6476-S-methyl *(M01)* and JAU 6476-desthio *(M04)*, JAU 6476-S-methyl samples were also analysed for prothioconazole and JAU 6476-desthio *(M04)* and JAU 6476-desthio samples were also analysed for traces of prothioconazole and JAU 6476-Smethyl *(M01)*.

The concentrations of JAU 6476-S-methyl *(M01)* and JAU 6476-desthio *(M04)* in the prothioconazole samples are summarised in Table 27.

The concentrations of prothioconazole and JAU 6476-desthio *(M04)* in all JAU 6476-S-methyl samples were below the LOD of the analytical method (2 µg/kg).

On days 3 and 7, one of the four replicates of the JAU 6476-desthio samples was found to contain residues of prothioconazole at concentrations below the LOQ of 6 µg/kg. In all remaining samples, no residues of prothioconazole or of JAU 6476-S-methyl *(M01)* could be detected.

Table 27 Concentrations of JAU 6476-S-methyl *(M01)* and JAU 6476 *(M04)* in the prothioconazole sample

Day	Recovered amounts in % of			Total recovered amounts (%)
	Prothioconazole	JAU 6476-S-methyl *(M01)*[a]	JAU 6476-desthio *(M04)*	
0	113	n.d.	n.d.	113
3	28.5	n.d.	22.2	50.7
7	30.3	n.d.	18.4	48.7
180	37.6	n.d.	25.3	62.9
420	32.8	n.d.	25.4	58.2

n.d. = concentrations of JAU 6476-S-methyl *(M01)* below the LOD of 2 µg/kg

[a] the concentrations of JAU 6476-desthio *(M04)* were converted to concentrations of prothioconazole equivalents by multiplication with the molecular factor of 1.103

To obtain more detailed understanding in the behaviour of prothioconazole under storage conditions, three additional sets of four samples each were spiked with the parent compound and analysed after 1, 3 and 15 hours storage at ambient temperature.

The results showed that prothioconazole could only be stabilised in frozen soil ($\leq$ -18 °C). At ambient temperature, the active substance dissipated quickly to JAU 6476-desthio *(M04)* and to traces of JAU 6476-S-methyl *(M01)*. The amounts that could be recovered from soil depended on the time between spiking of the soil samples and deep-freezing. The longer the samples were stored at room temperature, the lower were the recovered amounts of prothioconazole and the higher were the recovered amounts of JAU 6476-S-methyl *(M01)* and JAU 6476-desthio *(M04)*. Table 28 summarises the recovered amounts of prothioconazole and the two metabolites.

High losses of prothioconazole and its metabolites were found. After storage at room temperature for one hour, only 59% of the applied amount could be detected in the extract. In all samples, the losses (i.e., non-extractable residues etc.) were in the range of 40 to 50%. Similar effects could also be observed in the two aerobic soil metabolism studies (Gilges, 2000, amended 2001; and Hellpointner, 2001a). The fact that the amounts lost differed between studies may have been a result of different extraction and processing procedures.

Table 28 Behaviour of prothioconazole at storage in ambient conditions

Hours	Recovered amounts in % of			Total recovered amounts (%)
	Prothioconazole	JAU 6476-S-methyl *(M01)*	JAU 6476-desthio *(M04)*	
0 + 1 h	41.0	n.d.	17.9	58.9
0 + 3 h	35.5	n.d.	22.2	57.7
0 + 15 h	18.3	< LOQ	29.5	47.8

n.d. = concentrations of JAU 6476-S-methyl *(M01)* below the LOD of 2 µg/kg

< LOQ = concentrations of JAU 6476-S-methyl *(M01)* below the LOQ of 6 µg/kg

A study was conducted to determine the storage stability of 1*H*-1,2,4-triazole[3,5-^{14}C] in loamy sand under freezer (–25 °C) conditions (Shadrick, BA, Bloomberg, AM and Helfrich, KK, 1999). The recovery of 1,2,4-triazole averaged 96% from the day 0 samples and 94% from the 42 month samples. 1,2,4-Triazole stored under frozen conditions in loamy sand remained stable for 42 months. The total radioactive residues recovered from the samples were above 97% of the applied radioactivity throughout the study. The extracted radioactive residues for the treated samples ranged from 94% to 103% of the applied radioactivity. The bound radioactive residues increased to 4.2% of the applied radioactivity at the 42 month interval.

Crop rotation studies

Two confined rotational crop studies were conducted in wheat, Swiss chard and turnips using phenyl- and triazole-labelled parent compound.

In the study using phenyl-labelled prothioconazole, the parent compound was applied once at 578 g ai/ha. Crops of the first, second and third rotation were sown at day 28, 149 and 269, respectively. The plants were grown under natural conditions except that they were protected from rainfall and the soil surface was irrigated (Haas, M, 2001c).

The metabolism of triazole-labelled prothioconazole was investigated (Duah, FK and Kraai, MJ; 2004) in confined rotational crops following four applications to the soil in a large trough at an average rate of 204 g ai/ha/application. The rotational crops were planted at 30, 125 and 366 days after treatment (DAT). The crops were grown outside under natural weather conditions including rainfall.

The total radioactive residue (TRR) found in the different matrices of the confined rotational crops after application of phenyl- or triazole-labelled prothioconazole are summarised in Table 29.

Table 29 Comparison of the total radioactive residue (TRR) in rotational crop matrices following soil treatment with phenyl- and triazole labelled prothioconazole

Crop	Matrix	Rotation 1 (28 days)[a]			Rotation 2 (149 days)[a]			Rotation 3 (219 days)[a]		
		TRR (mg/kg)		Ratio[b]	TRR (mg/kg)		Ratio[b]	TRR (mg/kg)		Ratio[b]
		phenyl-label	triazole-label		triazole / phenyl	triazole-label		phenyl-label	triazole-label	
Wheat	forage	0.021	0.251	12	0.062	0.575	9	0.040	0.439	11
	hay	0.114	2.224	16	0.135	2.580	19	0.160	2.016	13
	straw	0.450	1.695	4	0.307	1.361	4	0.312	1.597	5
	grain	0.007	3.806	544	n.d.	4.136	–	n.d.	5.875	–
Swiss chard	leaves	0.039	0.188	5	0.053	0.047	5	0.021	0.129	6
Turnip	tops	0.046	0.131	3	0.028	0.507	18	0.036	0.084	2
	roots	0.043	0.059	1	0.031	0.442	14	0.015	0.061	4

[a] Seeds of rotation crops were sown after the soil treatment

[b] Ratio of triazole and phenyl-labelled radioactivity

The results of the two confined rotational crop studies revealed that prothioconazole was intensively metabolised.

In the study using phenyl-labelled prothioconazole the unchanged parent compound represented only < 0.005 mg/kg or ≤ 1% of any TRR. The main metabolite JAU 6476-desthio *(M04)* was detected in all RACs and amounted to 0.045 mg/kg in wheat straw of the first rotation. The hydroxy metabolites *(M14-M17)* also occurred in the rotational crop species. Furthermore, conjugation played an important role in the degradation of prothioconazole. The occurrence of some new but very minor polar metabolites (no single component > 0.05 mg/kg) is an indication that the composition of the TRR in rotational crops was also influenced by additional soil metabolites of prothioconazole.

A comparison of prothioconazole and its metabolites detected in rotational crops after application of prothioconazole (phenyl- and triazole-label) to soil in mg/kg eq ai is given in Tables 30 to 36, respectively.

Table 30 Distribution of the active substance and metabolites in wheat forage of rotation 1 to 3 from phenyl- and triazole-labelled prothioconazole confined rotational crop studies (mg ai eq/kg)

Parent compound / metabolite	Rotation 1		Rotation 2		Rotation 3	
label	*phenyl*	*triazole*	*phenyl*	*triazole*	*phenyl*	*triazole*
Prothioconazole						
Metabolites common to both labels:						
JAU 6476-sulfonic acid *(M02)*	< 0.001		0.002			
JAU 6476-triazolinone *(M03)*	< 0.001		< 0.001		< 0.001	
JAU 6476-disulfide *(M11)*	< 0.001		< 0.001		< 0.001	
JAU 6476-desthio *(M04)*	0.003		0.004	0.001	< 0.001	
JAU 6476-desthio-3-hydroxy *(M14)*	0.001		< 0.001		< 0.001	
JAU 6476-desthio-4-hydroxy *(M15)*	< 0.001		< 0.001			
JAU 6476-desthio-6-hydroxy *(M17)*			< 0.001			
JAU 6476-desthio-hydroxy-glucoside *(M21-23)*	0.001		0.009			
JAU 6476-desthio-α-hydroxy *(M18)*	< 0.001		0.001	0.004	< 0.001	
JAU 6476-desthio-α-acetoxy *(M19)*	< 0.001		0.002		< 0.001	
JAU 6476-desthio-dihydroxy-olefin-glucoside *(M64)*	0.003		0.019		0.017	
Metabolite specific to the phenyl-label:						
JAU 6476-benzylpropyldiol-glucoside *(M43)*	< 0.001		< 0.001			
Metabolites specific to the triazole-label:						
THP *(M30)*		0.087		0.184		0.155
Σ: TAA *(M29)* and THP *(M30)*				0.003		
TA *(M31)*		0.120		0.252		0.225
TAA *(M29)*		0.008		0.034		0.006
JAU 6476-triazolyl-ethanol *(M45)*		0.003		0.007		
JAU 6476-triazolyl-ethanol-glucoside *(M46)*		0.004		0.015		0.003
Total identified	0.010	0.222	0.040	0.500	0.021	0.389
Characterised	0.003	0.020	0.003	0.055	0.002	0.042
Unextracted	0.004	0.010	0.013	0.015	0.011	0.006
Total	0.021	0.251	0.062	0.575	0.040	0.438

Table 31 Distribution of the active substance and metabolites in wheat hay of rotation 1 to 3 from phenyl- and triazole-labelled prothioconazole confined rotational crop studies (mg ai eq/kg)

Parent compound / metabolite	Rotation 1		Rotation 2		Rotation 3	
label	*phenyl*	*triazole*	*phenyl*	*triazole*	*phenyl*	*triazole*
Prothioconazole						
Metabolites common to both labels:						
JAU 6476-sulfonic acid *(M02)*	0.013		0.009			
JAU 6476-triazolinone *(M03)*	0.001		0.001			
JAU 6476-disulfide *(M11)*	0.002		0.002		0.001	
JAU 6476-desthio *(M04)*	0.014	0.020	0.016	0.020	0.032[a]	
JAU 6476-desthio-3-hydroxy *(M14)*	0.003		0.001		0.002	
JAU 6476-desthio-4-hydroxy *(M15)*	0.004		0.002		0.003	
JAU 6476-desthio-hydroxy-glucoside *(M21-23)*	0.011		0.007		0.010	
JAU 6476-desthio-α-hydroxy *(M18)*	0.003	0.019	0.002	0.023	0.004	

Parent compound / metabolite	Rotation 1		Rotation 2		Rotation 3	
label	*phenyl*	*triazole*	*phenyl*	*triazole*	*phenyl*	*triazole*
JAU 6476-desthio-α-acetoxy *(M19)*	0.002		0.003		0.006	
JAU 6476-desthio-dihydroxy-olefin-glucoside *(M64)*	0.020		0.039		0.053	
Metabolites specific to the triazole-label:						
TA *(M31)*		0.720		0.846		0.719
THP *(M30)*		0.871		0.627		0.562
TAA *(M29)*		0.222		0.578		0.441
JAU 6476-triazolyl-ethanol *(M45)*		0.030		0.029		0.021
JAU 6476-triazolyl-ethanol-glucoside *(M46)*		0.045		0.060		0.030
Total identified	0.073	1.908	0.082	2.179	0.111	1.773
Additional characterised	0.006	0.238	0.009	0.329	0.016	0.068
Unextracted	0.020	0.076	0.029	0.011	0.009[a)]	0.045
Total	0.144	2.223	0.135	2.580	0.160	2.016

[a] after treatment with dioxane/HCl (9:1)

Table 32 Distribution of the active substance and metabolites in wheat straw of rotation 1 to 3 from phenyl- and triazole-labelled prothioconazole confined rotational crop studies (mg ai eq/kg)

Parent compound / metabolite	Rotation 1		Rotation 2		Rotation 3	
label	*phenyl*	*triazole*	*phenyl*	*triazole*	*phenyl*	*triazole*
Prothioconazole	0.004		0.001			
Metabolites common to both labels:						
JAU 6476-sulfonic acid *(M02)*	0.002		0.024		0.040	
JAU 6476-triazolinone *(M03)*	0.004		0.002		0.001	
JAU 6476-disulfide *(M11)*	0.007		0.005			
JAU 6476-desthio *(M04)*	0.045	0.014	0.026		0.018	
JAU 6476-desthio-3-hydroxy *(M14)*	0.017		0.004		0.003	
JAU 6476-desthio-4-hydroxy *(M15)*	0.012		0.004		0.007	
JAU 6476-desthio-6-hydroxy *(M17)*	0.007		0.002			
JAU 6476-desthio-hydroxy-glucoside *(M21-23)*	0.097		0.043		0.025	
JAU 6476-desthio-α-hydroxy *(M18)*	0.030	0.017	0.008	0.026	0.009	0.016
JAU 6476-desthio-α-acetoxy *(M19)*	0.009		0.013		0.009	
JAU 6476-desthio-dihydroxy-olefin-glucoside *(M64)*	0.055		0.044		0.056	
Metabolites specific to the phenyl-label:						
JAU 6476-benzylpropyldiol *(M09)*	0.010		0.002			
JAU 6476-benzylpropyldiol-glucoside *(M43)*					0.003	
Metabolites specific to the triazole-label:						
TA *(M31)*		0.358		0.197		0.407
THP *(M30)*		0.498		0.382		0.481
TAA *(M29)*		0.437		0.233		0.302
Σ: TAA *(M29)* and THP *(M30)*				0.041		
JAU 6476-triazolyl-ethanol *(M45)*		0.023		0.027		
JAU 6476-triazolyl-ethanol-glucoside *(M46)*		0.042		0.063		0.029
Total identified	0.299	1.389	0.180	0.969	0.171	1.235

Parent compound / metabolite	Rotation 1		Rotation 2		Rotation 3	
label	*phenyl*	*triazole*	*phenyl*	*triazole*	*phenyl*	*triazole*
Additional characterised	0.076	0.267	0.053	0.290	0.100	0.192
Unextracted	0.010[a]	0.006	0.020[a]	0.011	0.007[a]	0.006
Total	0.450	1.694	0.307	1.360	0.312	1.597

[a] unextracted (solids 3 after dioxan hydrolysis)

Table 33 Distribution of the active substance and metabolites in wheat grain of rotation 1 to 3 from phenyl- and triazole-labelled prothioconazole confined rotational crop studies (mg ai eq/kg)

Parent compound / metabolite	Rotation 1		Rotation 2		Rotation 3	
label	*phenyl*	*triazole*	*phenyl*[a]	*triazole*	*phenyl*[a]	*triazole*
Prothioconazole						
Metabolites common to both labels:						
JAU 6476-desthio *(M04)*	< 0.001					
JAU 6476-desthio-3-hydroxy *(M14)*	< 0.001					
JAU 6476-desthio-4-hydroxy *(M15)*						
JAU 6476-desthio-α-hydroxy *(M18)*	0.001					
Metabolites specific to the triazole-label:						
TA *(M31)*		2.264		2.372		3.940
THP *(M30)*		0.047		0.023		
TAA *(M29)*		1.116		0.957		1.485
Total identified	0.001	3.427		3.351		5.425
Additional characterised	0.001	0.285		0.135		0.285
Unextracted	0.005	0.011		0.021		0.014
Total	0.007	3.813		4.134		5.875

[a] grain sample material of rotation 2 and 3 was not analysed, because TRR value of rotation 1 was already well below the trigger value of 0.01 mg/kg

Table 34 Distribution of the active substance and metabolites in Swiss chard of rotation 1 to 3 from phenyl- and triazole-labelled prothioconazole confined rotational crop studies (mg ai eq/kg)

Parent compound / metabolite	Rotation 1		Rotation 2		Rotation 3	
label	*phenyl*	*triazole*	*phenyl*	*triazole*	*phenyl*	*triazole*
Prothioconazole			< 0.001			
Metabolites common to both labels:						
JAU 6476-sulfonic acid *(M02)*	< 0.001		0.001			
JAU 6476-triazolinone *(M03)*	0.001		0.001		< 0.001	
JAU 6476-disulfide *(M11)*	0.001		0.001		< 0.001	
JAU 6476-desthio *(M04)*	0.014	0.005	0.010	0.001	< 0.001	
JAU 6476-desthio-3-hydroxy *(M14)*	0.001		0.002		< 0.001	
JAU 6476-desthio-4-hydroxy *(M15)*	< 0.001		< 0.001			
JAU 6476-desthio-hydroxy-glucoside *(M21-23)*	0.004		0.006		0.001	
JAU 6476-desthio-α-hydroxy *(M18)*	< 0.001		0.001		< 0.001	
JAU 6476-desthio-dihydroxy-olefin-glucoside *(M64)*	0.007		0.006		0.004	
Metabolite specific to the phenyl-label:						
JAU 6476-benzylpropyldiol *(M09)*			< 0.001		< 0.001	

Parent compound / metabolite	Rotation 1		Rotation 2		Rotation 3	
label	*phenyl*	*triazole*	*phenyl*	*triazole*	*phenyl*	*triazole*
Metabolites specific to the triazole-label:						
TA *(M31)*		0.096		0.023		0.072
THP *(M30)*		0.060				0.038
Σ: TAA *(M29)* and THP *(M30)*				0.008		
TAA *(M29)*						0.001
JAU 6476-triazolyl-ethanol *(M45)*		0.014		0.002		0.002
Total identified	0.028	0.174	0.027	0.034	0.007	0.113
Additional characterised	0.005	0.008	0.014	0.001	0.005	
Unextracted	0.005	0.007	0.008	0.002	0.008	0.002
Total	0.039	0.188	0.053	0.047	0.021	0.129

Table 35 Distribution of the active substance and metabolites in turnip roots of rotation 1 to 3 from phenyl- and triazole-labelled prothioconazole confined rotational crop studies (mg ai eq/kg)

Parent compound / metabolite	Rotation 1		Rotation 2		Rotation 3	
label	*phenyl*	*triazole*	*phenyl*	*triazole*	*phenyl*	*triazole*
Prothioconazole	< 0.001					
Metabolites common to both labels:						
JAU 6476-triazolinone *(M03)*	< 0.001		< 0.001		< 0.001	
JAU 6476-disulfide *(M11)*			0.001		< 0.001	
JAU 6476-desthio *(M04)*	0.009	0.002	0.009	0.007	0.005	0.001
JAU 6476-desthio-3-hydroxy *(M14)*	0.005		0.001		< 0.001	
JAU 6476-desthio-4-hydroxy *(M15)*			0.001		< 0.001	
JAU 6476-desthio-6-hydroxy *(M17)*	< 0.001		0.001		< 0.001	
JAU 6476-desthio-hydroxy-glucoside *(M21-23)*	0.006		0.002		0.002	
JAU 6476-desthio-α-hydroxy *(M18)*	0.004		0.002	0.002	< 0.001	
JAU 6476-desthio-dihydroxy-olefin-glucoside *(M64)*	0.005		0.001		0.001	
Metabolites specific to the phenyl-label:						
JAU 6476-benzylpropyldiol *(M09)*	0.001		< 0.001			
JAU 6476-benzylpropyldiol-glucoside *(M43)*	0.001					
Metabolites specific to the triazole-label:						
Triazolylalanine = TA *(M31)*		0.048		0.411		0.052
Σ: TAA *(M29)* and THP *(M30)*		0.003		0.005		
JAU 6476-triazolyl-ethanol *(M45)*				0.002		
JAU 6476-triazolyl-ethanol-glucoside *(M46)*				0.001		
Total identified	0.031	0.053	0.017	0.428	0.009	0.053
Additional characterised	0.004	0.001	0.005	0.002	0.002	
Unextracted	0.008	0.003	0.008	0.012	0.003	0.002
Total	0.043	0.058	0.031	0.442	0.015	0.062

Table 36 Distribution of the active substance and metabolites in turnip tops of rotation 1 to 3 from phenyl- and triazole-labelled prothioconazole confined rotational crop studies (mg ai eq/kg)

Parent compound / metabolite	Rotation 1		Rotation 2		Rotation 3	
label	*phenyl*	*triazole*	*phenyl*	*triazole*	*phenyl*	*triazole*
Prothioconazole			< 0.001			
Metabolites common to both labels:						
JAU 6476-sulfonic acid *(M02)*	< 0.001					
JAU 6476-triazolinone *(M03)*	0.001		< 0.001			
JAU 6476-disulfide *(M11)*			< 0.001		0.001	
JAU 6476-desthio *(M04)*	0.008		0.002	0.005	0.005	
JAU 6476-desthio-3-hydroxy *(M14)*	0.001		< 0.001		0.001	
JAU 6476-desthio-4-hydroxy *(M15)*	0.002		0.001			
JAU 6476-desthio-6-hydroxy *(M17)*	0.001		< 0.001		< 0.001	
JAU 6476-desthio-hydroxy-glucoside *(M21-23)*	0.009		0.004		0.005	
JAU 6476-desthio-α-hydroxy *(M18)*	0.003	0.002	0.002	0.007	0.001	
JAU 6476-desthio-dihydroxy-olefin-glucoside *(M64)*	0.008		0.006		0.006	
Metabolites specific to the phenyl-label:						
JAU 6476-benzylpropyldiol *(M09)*	< 0.001					
JAU 6476-benzylpropyldiol-glucoside *(M43)*	0.001		0.001			
Metabolites specific to the triazole-label:						
TA *(M31)*		0.100		0.377		0.077
THP *(M30)*				0.035		
Σ: TAA *(M29)* and THP *(M30)*		0.009				
TAA *(M29)*				0.009		
JAU 6476-triazolyl-ethanol *(M45)*		0.004		0.020		
JAU 6476-triazolyl-ethanol-glucoside *(M46)*		0.004		0.015		
Total identified	0.036	0.119	0.016	0.468	0.018	0.077
Additional characterised	0.002	0.005	0.006	0.020	0.009	
Unextracted	0.008	0.005	0.006	0.020	0.009	0.003
Total	0.046	0.132	0.028	0.507	0.036	0.084

Field rotational crop trials were conducted at three locations (Georgia, Indiana, Kansas) to measure the magnitude of JAU6476 residues in field crops at 1, 4, 8 and 12- month plant-back intervals (PBIs) following the use of prothioconazole 480 SC on a target crop (Lemke VJ, Lenz CA, and Murphy JJ, 2004).

Each trial contained a control and a treated plot. Two foliar spray applications of prothioconazole 480 SC were made 14 (±2) days apart to bare soil in the treated plot at a target rate of 400 g ai/ha in target spray volumes ranging from 94 to 290 L/ha. The total application rate was about double of the highest prothioconazole label rate in the USA. Representative rotational crops were planted at each of three locations at all PBIs. The crops and their associated raw agricultural commodities (RACs) were wheat (forage, hay, grain and straw) to represent cereal grains; mustard greens (leaves) to represent leafy vegetables; and turnip (tops and roots) to represent root crops. All RACs were harvested at the earliest crop maturity.

The total residues of prothioconazole and JAU6476-desthio ('total prothioconazole derived residue') were quantified by HPLC-MS/MS (Gould, TJ, Timberlake, BC, Krolski, ME, Nguyen, TS, Moore E 2004) In the method, residues of JAU6476 are converted to JAU 6476-desthio and JAU

6476-sulfonic acid (both expressed as parent molar equivalents) and summed with unchanged JAU 6476-desthio (expressed as parent molar equivalents) to give a total prothioconazole-derived residue. The method for determining total prothioconazole residue was validated by measuring the recoveries of prothioconazole and JAU6476-desthio from wheat grain fortified at 0.02 mg/kg, from wheat forage, mustard greens, turnip tops and turnip roots fortified at 0.05 mg/kg, and from wheat hay and straw fortified at 0.10 mg/kg with each analyte, prior to and concurrent with the residue analyses.

Following two foliar spray applications of prothioconazole 480 SC to bare soil at a target rate of 400 g ai/ha, the total prothioconazole derived residue was less than the LOQ of 0.05 mg/kg (0.02 mg/kg for grain only) in all crop RACs at the 1-month PBI. No further analyses were conducted.

METHODS OF RESIDUE ANALYSIS

Analytical methods

The manufacturer provided validated methods for determination of residues in plants, animal tissue, milk and soil samples.

The principle of methods involves extraction steps using organic solvents plus varying proportions of water or water plus acid followed by different matrix dependant clean up steps. The final determination is carried out mostly by LC-MS/MS.

The methods validated for plant materials detect the prothioconazole and JAU-desthio (M04) (Table 37), while the methods for animal commodities measure JAU 6476-desthio, JAU 6476-desthio-3-hydroxy and JAU 6476-desthio-4-hydroxy, or prothioconazole, JAU 6476-desthio, JAU 6476-4-hydroxy and conjugates that can be converted to one of these compounds via acid hydrolysis.

Table 37 Analytical methods for the determination of prothioconazole and its metabolites

Principle of method	Substrate	Spike level	Q% [a]	LOQ (mg/kg)
Method for Plant and animal commodities suitable for Europe, Method 00086/M033 (Weeren, RD, Pelz, S, 2000)				
The extended DFG method S 19 was applied for the determination of JAU 6476-desthio in combination with GPC cleanup and GC/MS detection.	Tomato (fruit)	0.02–0.2	108–95	0.02
	Orange (whole fruit)	0.02–0.2	112–102	0.02
The relative standard deviation based on 4 replicate measurements ranged between 2.6 and 12%.	Wheat (green mass)	0.05–0.5	113–105	0.05
	Wheat (grain)			
The linearity, specificity and reproducibility were within the requirements of EU.	Wheat (straw)	0.02–0.2	93–86	0.02
	Rapeseed			0.05
	Milk	0.02–0.2	77–67	0.02
The method was independently validated (Class T, 2001).	Meat	0.01–0.1	84–87	0.01
	Egg	0.02–0.2	109–110	0.02
	Fat	0.02–0.2	105–98	0.02
		0.02–0.2	89–91	0.02
An analytical method for the determination of total residues of JAU6476 in plant matrices using LC/MS-MS [b] Method RPA JA/03/01 (Gould, TJ, Timberlake, BC, Krolski, ME, Nguyen T (2003); Gould, TJ, Timberlake, BC, Krolski, ME, Nguyen, TS, Moore E (2004)				
The crop matrices are extracted with a mixture of methanol (MeOH), 30% hydrogen peroxide (H_2O_2), and aqueous sodium bicarbonate ($NaHCO_3$) at 65 °C for two hours. *This extraction procedure converts prothioconazole to a mixture of JAU 6476-sulfonic acid and JAU 6476-desthio.* Residues of JAU 6476-desthio are extracted without change. Following the addition of a mixture of isotopically-labelled JAU 6476-sulfonic acid and JAU 6476-desthio internal standards, the sample extracts are purified by octadecyl solid	Barley hay	0.1	85	0.05
	Barley straw	0.1	79	0.05
	Barley grain	0.02	82	0.05
	Bean, dry	0.1	87	
	Canola seed	0.02–0.1	81–85	0.02
	Canola oil, refined	0.02	82	0.02
	Mustard greens			

Principle of method	Substrate	Spike level	Q% [a]	LOQ (mg/kg)
phase extraction (C-18 SPE). The purified analytes are analysed by high-performance liquid chromatography electrospray ionization/tandem mass spectrometry (LC-MS/MS). prothioconazole, JAU 6476-desthio, JAU 6476-sulfonic acid. The linearity, specificity and reproducibility were within acceptable range. The method was independently validated in peanut meat and wheat forage. (Clark, JA, 2004)	Pea, dry	0.05–1	84–82	0.05
	Peanut hay	0.1–1.0	101–93	0.05
	Peanut nutmeat	0.02–0.1	83–85	0.02
	Peanut oil, refined	0.02	77	0.02
	Peanut butter	0.02–0.1	84–87	0.02
	Rice straw			
	Rice grain	0.02	87	0.1
	Soybean seed	0.05–0.35	94–73	0.02
	Soybean meal	0.05	83	0.05
	Soybean, refined oil	0–05	77	0.05
		0.05	80	0.05
	Turnip tops	0.05–1.0	78–82	
	Turnip roots	0.05–1.0	79–74	0.05
	Wheat forage	0.05–1.0	83–90	0.05
	Wheat hay	0.02–0.2	72–82	0.05
	Wheat straw	0.02–0.2	81–85	0.05
	Wheat grain	0.02–0.2	72–84	0.02
	Wheat bran	0.02–0.2	77–84	0.05
	Wheat flour	0.02–0.2	79–92	0.05
	Wheat germ	0.02–0.2	89–91	0.05
	Wheat middlings	0.02–0.2	72–84	0.05
	Wheat shorts	0.02–0.2	77–84	0.05
		0.02–0.2	79–92	0.02
		0.02–0.2	89–91	0.02
Determination of residues of JAU6476-3-hydroxy-desthio, JAU6476-4-hydroxy-desthio, and JAU6476-desthio in/on matrices of animal origin by HPLC-MS/MS (Method 00655) (Heinemann, O 2001)				
Homogenized sample materials of meat, liver and kidney were extracted twice with a mixture of acetonitrile/water, and centrifuged. The combined supernatants were evaporated to the aqueous remainder, which was diluted with water, acidified with 5 N HCl solutions and refluxed for two h. This hydrolysis step was performed to convert non-aromatic precursor compounds and glycosidic-bound analogues into JAU 6476-desthio-3-hydroxy and JAU 6476-desthio-4-hydroxy. An aliquot was neutralized and purified on a ChemElut cartridge. The concentrated purified extract was chromatographed by HPLC on a silica-based C18-column and determined by a triple-stage mass spectrometer with a TurboIonSpray interface (ESI:) operated in the positive ion mode (RP-HPLC-ESI-MS/MS). In this mode the protonated molecular ions were separated and impulsed immediately with nitrogen to its characteristic productions. The product ions were used for quantification. Milk samples were hydrolysed and purified directly after dilution with water. The extracts of fat samples were partitioned against n-hexane twice. Finally, the acetonitrile/water phase was evaporated to the aqueous remainder, hydrolysed and purified the same way as the other matrices. The extraction approach as used in the present method was shown to be quantitative in terms of aged (labelled) residues originating from a goat metabolism study.	JAU 6476 desthio-3-hydroxy			
	Milk	0.01–0.1	98–99	0.01
	Meat	0.01–0.1	98–99	0.01
	Liver	0.01–0.1	96	0.01
	Kidney	0.01–0.1	96	0.01
	Fat	0.01–0.1	88–97	0.01
	JAU 6476 desthio-4-hydroxy			
	Milk	0.01–0.1	103	0.01
	Meat	0.01–0.1	99–101	0.01
	Liver	0.01–0.1	109	0.01
	Kidney	0.01–0.1	103–104	0.01
	Fat	0.01–0.1	91–99	0.01
	JAU 6476 desthio			
	Milk	0.01–0.1	93	0.01
	Meat	0.01–0.1	96–97	0.01
	Liver	0.01–0.1	89–90	0.01
	Kidney	0.01–0.1	91–92	0.01
	Fat	0.01–0.1	84	0.01

Principle of method	Substrate	Spike level	Q% [a]	LOQ (mg/kg)
Determination of residues of JAU6476-3-hydroxy-desthio, JAU6476-4-hydroxy-desthio, and JAU6476-desthio in milk by HPLC-MS/MS (Method 00655/001), (Heinemann, O 2001a)				
The original method (00655) was validated at lower LOQ of 0.004 mg/kg. JAU 6476 desthio-3-hydroxy JAU 6476 desthio-4-hydroxy JAU 6476 desthio	Milk	 0.004–0.04 0.004–0.04 0.004–0.04	 98–101 96–100 98	0.004
Independent laboratory validation of Bayer Methods 00655 and 00655/M001 for the determination of residues of JAU6476-3-hydroxy-desthio, JAU6476-4-hydroxy-desthio, and JAU6476-desthio in/on matrices of animal origin by HPLC-MS/MS (Method 00655/02 (Dubey, L, 2001)				
JAU 6476 desthio-3-hydroxy JAU 6476 desthio-4-hydroxy JAU 6476 desthio	Milk	0.004–0.04 0.004–0.04 0.004–0.04	106–104 107–104 105	0.004
JAU 6476 desthio-3-hydroxy JAU 6476 desthio-4-hydroxy JAU 6476 desthio	Meat	0.01–0.1 0.01–0.1 0.01–0.1	94–97 94–96 92	0.01
JAU 6476 desthio-3-hydroxy JAU 6476 desthio-4-hydroxy JAU 6476 desthio	Liver	0.01–0.1 0.01–0.1 0.01–0.1	99–89 100–89 85–101	0.01
Analytical method 00655/M002 for the determination of residues of JAU6476 desthio, JAU6476-3-hydroxy-desthio and JAU6476-4-hydroxy-desthio in/on matrices of animal origin by HPLC-MS/MS Method (00655/002) (Freitag, T, 2007)				
The modification of methods 00655 and 00655/M001 was performed to provide additional validation data (second transition) for confirmation of JAU 6476-desthio-3-hydroxy, JAU 6476-desthio-4-hydroxy and JAU 6476-desthio in matrices of animal origin by HPLC-MS/MS with the same extraction procedure as described in Bayer Method No. 00655.	JAU 6476 desthio-3-hydroxy m/z 328→70, or →141			
	Milk	0.04–0.04	88–94	0.004
	Meat	0.01–0.1	93–91	0.01
	Liver	0.01–0.1	90	0.01
	Kidney	0.01–0.1	91–90	0.01
	Fat	0.01–0.1	93–91	0.01
	JAU 6476 desthio-4-hydroxy m/z 328→70, or →141			
	Milk	0.004–0.04	89–92	0.01
	Meat	0.01–0.1	92–90	0.01
	Liver	0.01–0.1	90–91	0.01
	Kidney	0.01–0.1	93–89	0.01
	Fat	0.01–0.1	95–89	0.01
	JAU 6476 desthio m/z 312→70, or →125			
	Milk	0.004–0.04	80–91	0.004
	Meat	0.01–0.1	91–89	0.01
	Liver	0.01–0.1	86–88	0.01
	Kidney	0.01–0.1	80–90	0.01
	Fat	0.004–0.04	89–88	0.01
Independent laboratory validation of Bayer Crop Science method 00655/M002 for the determination and confirmation of residues of JAU6476-desthio, JAU6476-3-hydroxy-desthio and JAU6476-4-hydroxy-desthio in/on matrices of animal origin by HPLC-MS/MS (Schwarz T, Class T, 2007)				
The HPLC-MS/MS method 00655/M002 was validated for the determination of JAU 6476-desthio-3-hydroxy, JAU 6476-desthio-4-hydroxy, and JAU 6476-desthio residues in cows' milk, bovine meat, liver and fat.	JAU 6476 desthio-3-hydroxy m/z 328→70, or →141			
	Milk	0.04–0.04	82–90	0.004
	Meat	0.01–0.1	84–91	0.01
	Liver	0.01–0.1	88–90	0.01
	Fat	0.01–0.1	71–90	0.01
	JAU 6476 desthio-4-hydroxy m/z 328→70, or →141			

Principle of method	Substrate	Spike level	Q% [a]	LOQ (mg/kg)
	Milk	0.04–0.04	82–94	0.004
	Meat	0.01–0.1	84–91	0.01
	Liver	0.01–0.1	86–90	0.01
	Fat	0.01–0.1	91–90	0.01
	JAU 6476 desthio m/z 312→70, or →125			
	Milk	0.04–0.04	82–90	0.004
	Meat	0.01–0.1	82–89	0.01
	Liver	0.01–0.1	89–88	0.01
	Fat	0.01–0.1	73–90	0.01
Method for the determination of JAU 6476, JAU 6476-Desthio, and JAU 6476-4-hydroxy residues in various bovine matrices by LC-MS/MS, (Version 2) Report No. 200537, (Moore SM and Harbin AM, 2004)				
The HPLC-MS/MS method is capable of determining prothioconazole, JAU 6476-desthio, JAU 6476-4-hydroxy, and conjugates that can be converted to one of these compounds via acidic hydrolysis. Samples of bovine liver, kidney, and muscle are extracted with acetonitrile (ACN)/water containing 250 mg/ml L-cysteine HCl (4:1 v/v). An *internal standard solution (stable isotope-labelled analogues of each analyte of interest) is added to the extract*. Fat samples are extracted with n-hexane and then with a mixture of ACN/water containing 250 mg/ml L-cysteine HCl (4:1 v/v) and acetone; the combined extracts are allowed to separate, and internal standard solution is added to the aqueous phase. Samples of milk and cream are mixed with internal standard solution directly. For all matrices, the extract/sample is hydrolysed with 5N HCl under reflux for two hours, and the hydrolysate is partitioned with methylene chloride and acetone. The organic phase is concentrated to an aqueous remainder, mixed with ACN and water, and analysed by LC-MS/MS.	Prothioconazole, negative ion mode, m/z 342→ 100			
	Milk	0.005–0.01	105–101	0.005
	Skim milk	0.01	102	0.01
	Milk cream	0.01	102	0.01
	Meat	0.01	92	0.01
	Liver	0.01–0.6	99–91	0.01
	Kidney	0.01–0.8	80–103	0.01
	Fat	0.05–0.8	87–92	0.05
	JAU 6476-desthio, positive ion mode 312→ 70			
	Milk	0.005–0.01	105	0.005
	Skim milk	0.01	99	0.01
	Milk cream	0.01	107	0.01
	Meat	0.01	103	0.01
	Liver	0.01–0.6	113	0.01
	Kidney	0.01–0.8	10–105	0.01
	Fat	0.05–0.8	94–103	0.05
	JAU 6476-4-hydroxy, negative ion m., m/z 358→ 100			
	Milk	0.005–0.01	94–80	0.005
	Skim milk	0.01	86	0.01
	Milk cream	0.01	67	0.01
	Meat	0.01	99	0.01
	Liver	0.01–0.6	96–103	0.01
	Kidney	0.01–0.8	95–100	0.01
	Fat	0.05–0.8	81–85	0.05
Determination of JAU6476, JAU6476-desthio, and JAU6476-4-hydroxy in bovine milk and liver Document No. M-001598-01-1 (Reed, DE, 2004)				
The method developed by Moore and Harbin was validated in an independent laboratory.	Prothioconazole, negative ion mode, m/z 342→ 100			
	Milk	0.005–0.5	99–103	0.005
	Liver	0.01–0.5	82–93	
	JAU 6476-desthio, positive ion mode 312→ 70			
	Milk	0.005–0.5	97–103	0.005
	Liver	0.01–0.5	88–104	0.01
	JAU 6476-4-hydroxy, negative ion m., m/z 358→ 100			
	Milk	0.005–0.5	100–104	0.005
	Liver	0.01–0.5	82–95	0.01

[a] Average recoveries obtained from 2–4 replicate measurements

[b] The recovery ranges refer to prothioconazole, the recoveries for JAU 6476-desthio ranged from 87% to 108% (typically 95–101%), and for JAU 6476-sulfonic acid in canola, peanut and wheat from 78 to 112% (typically between 90–95%)

For supervised trials specialized methods were used which are summarized in Table 38.

Table 38 Specific methods for determination of prothioconazole and its selected metabolites

Principle of method	Substrate	Spike level [a]	Q% [b]
Determination of residues of JAU6476-sulfonic acid and JAU6476-desthio in/on cereals and canola by HPLC-MS/MS Method 00647, (MR 458600) (Heinemann, O, 2001b)			
JAU 6476-desthio and JAU sulfonic acid were extracted from the homogenized samples with an acetonitrile/water mixture. After filtration the extract was diluted for measurement by HPLC-MS/MS. The analyte was chromatographed by reversed-phase HPLC on a silica-based C18-column. A triple-stage mass spectrometer with a TurboIonSpray electrospray interface (ESI:) operated in the positive ion mode was used for determining JAU 6476-desthio. under MRM (multi reaction monitoring) conditions. (JAU 6476-desthio: m/z = 312 → m/z = 70). The product ion was used for quantification. Calibration was performed against internal (stable) labelled bracketing standard.	JAU6476-sulfonic acid: m/z = 390 –> m/z = 354		
	Wheat grain	0.01–0.1	107–100
	Wheat forage	0.05–5.0	96–102
	Wheat straw	0.05–5.0	98–100
	Barley grain	0.01–0.1	103–102
	Barley forage	0.05–5.0	89–97
	Barley straw	0.05–5.0	100–93
	Barley brewing malt	0.02–0.2	106–103
	Canola seed	0.01–0.1	91–94
	Canola forage	0.05–5.0	95–102
	Canola straw	0.05–5.0	94–100
	Canola pod	0.05–0.5.0	102–99
	JAU6476-desthio: m/z = 312 –> m/z = 70)		
	Wheat grain	0.01–0.1	103–100
	Wheat forage	0.05–5.0	108–98
	Wheat straw	0.05–5.0	101–99
	Barley grain	0.01–0.1	100
	Barley forage	0.05–5.0	103–97
	Barley straw	0.05–5.0	102–97
	Barley brewing malt	0.02–0.2	97–99
	Canola seed	0.01–0.1	91–94
	Canola forage	0.05–5.0	104–99
	Canola straw	0.05–5.0	101–99
	Canola pod	0.05–0.5.0	108–97
Supplement E001 to method 00647 for the determination of residues of Prothioconazole-desthio in/on broccoli, Brussels sprout, cauliflower, head cabbage, leek, tomato, sugar beet, pea and spinach by HPLC-MS/MS Method: 00647/E001 (MR-066/03) (Freitag T, 2004)			
Method 00647 was extended to determine JAU 6476-desthio in/on plant matrices by HPLC-MS/MS.	Broccoli curd Brussels sprout Cauliflower curd Head Cabbage red, Savoy Cabbage, head Leek shoot Tomato fruit Sugar beet root Sugar beet leaf with root collar Pea dried Pea pod Pea with pod Pea without pod Spinach leaves	0.01,0.1, 5.0	96 (3.5) 95 (4.1) 98 (2.8) 99 (2.8) 97 (7.6) 101 (4.3) 100 (4.0) 98 (3.5) 99 (5.2) 96 (1.7) 98 (4.1) 99 (1.5 92 (6) 97 (4.2)

Principle of method	Substrate	Spike level [a]	Q% [b]
Determination of residues of JAU6476 and desthio-JAU6476 in/on cereals by HPLC-MS/MS Method: 00598 (MR 401/99) (Heinemann, O, 2000)			
The prothioconazole and JAU 6476-desthio were extracted from cereal samples with an acetonitrile/water mixture in the presence of cysteine hydrochloride solution. The extract was cleaned up by liquid-liquid partition using n-hexane (saturated with acetonitrile) and dichloromethane. The analytes were determined with HPLC-MS/MS in the multiple-reaction-monitoring mode (MRM mode). The analytes were quantified against known amounts of external bracketing matrix-matched standard.	Prothioconazole		
	Wheat grain	0.01, 0.01	101 (5.4)
	Wheat straw	0.05, 0.5, 5.0	(89 (6.1)
	Wheat forage	0.05, 0.5, 5.0	99 (4.6)
	Barley grain	0.01, 0.01	98 (4.3)
	Barley straw	0.05, 0.5, 5.0	91 (5.5)
	Barley forage	0.05, 0.5, 5.0	82 (11.5)
	JAU6476-desthio		
	Wheat grain	0.01, 0.01	90 (7.5)
	Wheat straw	0.05, 0.5, 5.0	92 (2.3)
	Wheat forage	0.05, 0.5, 5.0	91 (4.5)
	Barley grain	0.01, 0.01	83 (4.0)
	Barley straw	0.05, 0.5, 5.0	92 (3.9)
	Barley forage	0.05, 0.5, 5.0	11.8)

[a] The lowest spike level (mg/kg) indicated is equal to the LOQ.

[b] Average of 3–5 replicate tests at each level with minimum and maximum values observed or RSD of recoveries (in brackets)

Several methods were presented which were validated for the determination of the residues of prothioconazole and its metabolites in soil. The major characteristics of the methods are summarized in Table 39.

Table39 Summary of methods for determination of residues of prothioconazole and its selected metabolites in soil

Method Number	Characteristics of the method	Reference
00610	The method was validated for determination of prothioconazole, JAU 6476-S-methyl *(M01)* and JAU 6476-desthio *(M04)* in soil. Soil samples were extracted with a mixture of acetonitrile/water/cysteine hydrochloride monohydrate. Internal standard solution was added to a portion of the filtered solution and the final volume was made up with water. Identification and quantification of all analytes was done by HPLC-MS/MS in the multiple-reaction-monitoring (MRM) mode. Isotopically labelled internal standards (JAU 6476-triazole-^{15}N, ^{13}C, JAU 6476-S-methyl-d_3, ^{13}C and JAU 6476-desthio-triazole-^{15}N, ^{13}C) were used to compensate for possible matrix effects in the MS/MS-detector. The LOQ was 0.006 mg/kg. The mean recoveries of the method over all single values at 6, 50 and 200 µg/kg fortification levels were 94.9% for prothioconazole (RSD = 8.0%), 100.6% for JAU 6476-S-methyl (RSD = 6.5%) and 102.4% for JAU 6476-desthio (RSD = 7.6%).	Schramel, O (2000)
00610/M001	The HPLC-MS/MS method applies a second MRM transition for confirmation. The mean recoveries over all single values (6 and 60 µg/L) were 104% for prothioconazole (m/z 326.1) (RSD = 2.1%), 103% for prothioconazole (m/z 189.1) (RSD = 2.5%), 102% for JAU 6476-desthio *(M04)* (m/z 125.0) (RSD = 2.3%) and 102% for JAU 6476-desthio (m/z 70.2) (RSD =2.9%). The blank values of all control samples were below 2.0 µg/kg for prothioconazole and JAU 6476-desthio *(M04)*. The LOQ is 0.006 mg/kg.	Brumhard, B (2005)

Method Number	Characteristics of the method	Reference
00086/M038	DFG Method S 19 (extended revision) for the GC/MS determination of the residues of JAU 6476-desthio *(M04)* in soil was validated. For quantification fragment ion m/z 188 was used. For verification the ions m/z 186 and m/z 125 were selected. The LOQ was 0.01 mg/kg. Applying matrix matched calibration overall mean recovery was 97% (RSD 11%, n = 10) at 0.01 and 0.10 mg/kg levels.	Steinhauer, S (2001)
M-000691-01-1	Prothioconazole, JAU 6476-S-methyl *(M01)*, JAU 6476-desthio *(M04)* and JAU 6476-thiazocine *(M12)* was determined in soil and sediment using high-performance liquid chromatography electrospray tandem mass spectrometry (LC-MS/MS). The soil samples were extracted with acetonitrile/water/cysteine hydrochloride (800/200/0.5, v/v/w) at room temperature in a mechanical shaker for an hour. The centrifuged extracts (4 ml) were transferred to a culture tube and heavy isotope internal standards were added. An aliquot of the extract (700 µl) was added to a HPLC vial and diluted with 300 µL of water. The resultant solution was analysed by LC-MS/MS, and quantitation was done against known amount of heavy isotopic internal standards. The LOQ was 0.01 mg/kg. The average recoveries of prothioconazole, JAU 6476-S-methyl, JAU 6476-desthio and JAU 6476-thiazocine fortified at 0.01 mg/kg were 98.3, 101.4, 103.1 and 99.7%, respectively. The average recoveries of prothioconazole, JAU 6476-S-methyl, JAU 6476-desthio and JAU 6476-thiazocine fortified at 0.1 mg/kg were 97.7, 93.5, 95.6 and 97.0%, respectively.	Lam, CK (2004)
M-107510-01-1	Independent laboratory validation of method M-000691-01-1 for prothioconazole, JAU 6476-S-methyl *(M01)*, JAU 6476-desthio *(M04)* and JAU 6476-thiazocine *(M12)*. The LOQ was 0.01 mg/kg. At 0.01 mg/kg and 0.1 mg/kg the average recoveries for prothioconazole, M01, M04 and M12 were, respectively: 88–81%, 93–90%, 93–91% and 96–88%.	South, NL (2003)
01069	1,2,4-triazole *(M13)* was determined in soil and sediment using high-performance liquid chromatography tandem with mass spectrometry (LC-MS/MS). LOQ was 0.01 mg/kg. Average recoveries of 1,2,4-triazole at 0.01 mg/kg ranged from 96.8 to 101.7%, and at 0.1 mg/kg the range was 82.5 to 87.1%.	Murphy, IM, Leimkuehler, WM, Moore, S (2004), amended by Freitag, T (2007)
M-107550-01-1	Method 01069 was validated in an independent laboratory for the determination of 1,2,4-triazole (M13) in soil. LOQ was 0.01 mg/kg. The recovery ranges between 87–99% at 0.01 and 0.1 mg/kg spike levels.	South, NL (2003a)
00610	The method was validated for determination of prothioconazole, JAU 6476-S-methyl *(M01)* and JAU 6476-desthio *(M04)* in soil. Soil samples were extracted with a mixture of acetonitrile/water/cysteine hydrochloride monohydrate. Internal standard solution was added to a portion of the filtered solution and the final volume was made up with water. Identification and quantification of all analytes was done by HPLC-MS/MS in the MRM mode. Isotopically labelled internal standards (JAU 6476-triazole-^{15}N, ^{13}C, JAU 6476-S-methyl-d_3, ^{13}C and JAU 6476-desthio-triazole-^{15}N, ^{13}C) were used to compensate for possible matrix effects in the MS/MS-detector. The LOQ was 0.006 mg/kg. The mean recoveries of the method over all single values at 6, 50 and 200 µg/kg fortification levels were 94.9% for prothioconazole (RSD = 8.0%), 100.6% for JAU 6476-S-methyl (RSD = 6.5%) and 102.4% for JAU 6476-desthio (RSD = 7.6%).	Schramel, O (2000)

Stability of residues in stored analytical samples

Freezer storage stability of JAU 6476-desthio was examined in wheat and in canola (seed, pod and straw), spinach (leaves), sugar beet (body, and leaf with root collar), tomato (fruit) and field pea (field pea dried). The stability of total residues determined according to the US residue definition were tested in tomato fruit, mustard greens, canola, turnip root, wheat forage, hay, grain and straw. The results of the studies are summarised below.

The stability of JAU 6476-desthio during frozen storage in wheat matrices were tested for a period of 18 and 36 months (Heinemann, O 2001c, Heinemann, O, 2003).

Fresh bulk material of wheat (green material, grain and straw) was fortified with JAU 6476-desthio and the level of fortification was determined on day-0 analysis. The samples were stored at temperatures of –18 °C or below, and were analysed at intervals of 0, 30, 60, 90, 120, 180, 360 and 540 days. Residues of JAU 6476-desthio were determined according to method 00598 (Heinemann, 2000).

The method was validated by recovery experiments at each storage interval by spiking control samples with JAU6476-desthio (concurrent recoveries). The control samples were fortified at 0.50 to 1.5 mg/kg for forage, 0.10 to 0.15 mg/kg for grain and 0.50 to 0.75 mg/kg for straw samples. The recovery rates for JAU6476-desthio were in the range of 79 to 106% (overall mean 90%, rsd 6.1%, *n*=49). In addition, at each interval, recoveries at the respective LOQs were performed (0.01 mg/kg for grain, 0.05 mg/kg for forage and straw; recoveries for method validation). The recovery rates for JAU6476-desthio were in the range of 67 to 108% (overall mean 88%, rsd 7.8%, *n*=49). The results are summarised in Table 40.

Table 40 Percentage of the day-0 concentration of JAU 6476-desthio in wheat matrices after deep-frozen storage for a period of over three years

Sample material	Storage interval (days)	Concurrent Recoveries [a]		JAU 6476-desthio	
		Levels (mg/kg)	Mean%	Mean (%)[b]	RSD
Forage	0	0.50	93	100 [b]	8.4
	34	0.50	92	106	9.8
	57	0.50	93	106	2.2
	105	0.50	93	102	7.1
	121	0.50	100	103	10.4
	169	0.50	100	102	3.6
	393	1.5	87	93	5.1
	576	1.5	87	98	4.2
	763	1.5	87	93	2.3
	1022	1.5	86	113	4.1
	1126	1.5	89	117	7.5
Grain	0	0.10	85	100 [c]	3.5
	23	0.10	81	94	4.3
	53	0.10	90	101	5.1
	92	0.10	92	100 [c]	0.6
	122	0.10	98	114	4.7
	197	0.10	84	98	13.7
	352	0.15	87	105	10.4
	535	0.15	86	97	5.1
	731	0.01	76	86	19.9
	975	0.01	86	97	0.0
	987	0.01	–	93	12.9
	1088	0.01	75	94	6.7
Straw	0	0.50	90	100 [c]	2.7
	34	0.50	89	101	2.0
	57	0.50	89	101	5.7
	96	0.50	91	100	2.9
	120	0.50	93	114	7.7
	167	0.50	93	103	0.9
	392	0.75	–[d]	98	2.7
	575	0.75	81	93	3.3
	762	0.05	96	101	2.5

Sample material	Storage interval (days)	Concurrent Recoveries [a]		JAU 6476-desthio	
		Levels (mg/kg)	Mean%	Mean (%)[b]	RSD
	1016	0.05	89	101	4.6
	1128	0.05	90	99	3.3

[a] Mean of recovery rates from two freshly fortified samples

[b] Mean of recovery rates from three stored samples The values presented in the tables were neither corrected for the concurrent recoveries at the respective intervals nor for the recoveries at day 0.

[c] Mean of recovery rates from three stored samples except where 5 single values were reported

[d] Mean of recovery rates from two freshly fortified samples except where one single value was reported

The stability of JAU 6476-desthio residues was tested under deep-frozen storage conditions in canola (seed, pod and straw), spinach (leaves), sugar beet (body, and leaf with root collar), tomato (fruit) and field pea (field pea dried) (Freitag T, 2005). Individual aliquots of the homogenized sample materials were fortified with 0.50 mg/kg of prothioconazole-desthio. The fortified samples were stored in a freezer at about minus 18 °C or below for up to ca. 24 months. Control samples that had not been fortified with prothioconazole-desthio were stored under the same conditions to allow procedural recovery determination from freshly fortified samples. Residues of JAU 6476-desthio were determined by HPLC-MS/MS Three stored fortified samples (except for the day 0 samples where five samples have been spiked with prothioconazole-desthio), one stored control sample, and two stored control sample were analysed after nominal storage periods of 0, 2, 4, 6, 12 and 24 months. The analytical method was validated prior to analysis by running a set of recoveries at the limit of quantification (0.01 mg/kg).

Table 41 Percentage of the day-0 concentration of JAU 6476-desthio in plant matrices after deep-frozen storage for a period of over two years

Sample material	Storage interval (months)	Concurrent Recoveries % [a]	JAU 6476-desthio[b]	
			% of day 0	RSD%
Canola (Seed)	0	90	100	5.4
	2	88	103	2.7
	4	88	105	1.7
	6	86	98	1.7
	12	89	105	2.9
	24	85	98	0.9
Canola (Pod)	0	100	100	2.4
	2	102	103	0.3
	4	100	107	4.0
	6	99	101	1.1
	12	102	102	0.3
	24	99	99	0.6
Canola (Straw)	0	98	100	2.2
	2	100	95	2.5
	4	100	101	2.4
	6	98	95	1.1
	12	98	97	0.8
	24	97	96	1.3
Spinach (Leaves)	0	105	100	2.9
	2	102	97	1.7
	4	98	97	1.6
	6	98	97	1.7
	12	104	100	2.1
	24	98	94	0.5

Sample material	Storage interval (months)	Concurrent Recoveries % [a]	JAU 6476-desthio[b]	
			% of day 0	RSD%
Sugar Beet (body)	0	95	100	2.4
	2	96	102	0.5
	4	98	102	0.6
	6	97	103	1.7
	12	98	105	0.9
	24	96	100	0.8
Sugar Beet (leaf with root collar)	0	93	100	3.0
	2	97	102	2.8
	4	95	101	5.1
	6	101	99	2.7
	12	101	103	1.6
	24	96	98	1.9
Tomato (fruit)	0	101	100	1.0
	2	102	98	1.4
	4	99	103	1.2
	6	106	100	2.8
	12	100	101	1.6
	24	99	96	1.9
Field pea (dried)	0	95	100	1.8
	2	90	95	3.3
	4	92	97	3.5
	6	94	96	2.1
	12	100	107	1.6
	24	90	98	1.8

[a] Mean of recovery rates from two freshly fortified samples (%)

[b] The values presented in the tables were neither corrected for the concurrent recoveries at the respective intervals nor for the recoveries at day 0.

Individual samples of tomato fruit, mustard greens, canola seed, turnip root and wheat (hay, straw, forage and grain) were fortified with prothioconazole and JAU6476-desthio (Lemke, VJ and Murphy, JJ 2004). The fortification standard was prepared at 0.2 mg/kg with a mixed standard containing prothioconazole and JAU6476-desthio at a 1:1 ratio as expressed in parent equivalents (0.10 mg/kg of each analyte).

Thirty-six months after initiation of the study (35 months for wheat forage), all matrices were analysed for determining the total prothioconazole derived residue in plants. In the method, residues of prothioconazole were converted to JAU 6476-desthio and JAU 6476-sulfonic acid (both expressed as parent molar equivalents) and summed with unchanged JAU 6476-desthio (expressed as parent molar equivalents) to give a total prothioconazole derived residue.

Each analysis set consisted of duplicate control samples, triplicate stability samples, duplicate concurrent recoveries fortified with 0.100 mg/kg prothioconazole, duplicate concurrent recoveries fortified with 0.100 mg/kg JAU6476-desthio and duplicate concurrent recoveries fortified with a mixture of 0.100 mg/kg each of prothioconazole and JAU6476-desthio.

Table 42 Summary of freezer stability data for prothioconazole residues

Matrix	Storage period (days)	Total residue found (mg/kg)[a]	Proportion of total residue in stored sample (%)[b]	Concurrent Percent Recovery [c]
Wheat Forage	1049	0.158	78	85
Wheat Forage	1049	0.162	80	85
Wheat Forage	1049	0.159	79	85

Matrix	Storage period (days)	Total residue found (mg/kg)[a]	Proportion of total residue in stored sample (%)[b]	Concurrent Percent Recovery [c]
Wheat Hay	1078	0.171	84	92
Wheat Hay	1078	0.181	89	92
Wheat Hay	1078	0.176	87	92
Wheat Straw	1077	0.176	87	93
Wheat Straw	1077	0.173	85	93
Wheat Straw	1077	0.169	84	93
Wheat Grain	1077	0.134	66	97
Wheat Grain	1077	0.139	69	97
Wheat Grain	1077	0.127	63	97
Tomato Fruit	1079	0.152	76	97
Tomato Fruit	1079	0.158	79	97
Tomato Fruit	1079	0.156	78	97
Mustard Greens	1078	0.171	85	96
Mustard Greens	1078	0.169	84	96
Mustard Greens	1078	0.164	82	96
Turnip Roots	1078	0.164	82	99
Turnip Roots	1078	0.163	81	99
Turnip Roots	1078	0.167	83	99
Canola Seed	1079	0.163	81	98
Canola Seed	1079	0.161	80	98
Canola Seed	1079	0.161	80	98

[a] All samples were fortified with prothioconazole and JAU6476-desthio at 0.200 mg/kg (0.10 mg/kg each analyte).

[b] Residues were corrected for control interferences prior to calculating the percent recovery, but not for concurrent recoveries.

[c] Each analysis set consisted of duplicate controls, triplicate stability samples, duplicate concurrent recoveries fortified with 0.100 mg/kg JAU6476, duplicate concurrent recoveries fortified with 0.100 mg/kg JAU6476 desthio, and duplicate concurrent recoveries fortified with 0.100 mg/kg each prothioconazole and JAU6476-desthio. Concurrent percent recovery is the average of the duplicate fortifications of the mixed prothioconazole /JAU6476-desthio recoveries.

The stability of total residues was studied in/on tomato fruit and paste, canola seed and oil, turnip roots, wheat (forage, hay, straw, grain, bran, and flour) and mustard greens (Duah FK, 2005) Analysis of samples was conducted at day-zero and at nominal intervals of two months and four months. Additionally, canola, barley, peas and wheat samples from the prothioconazole field crop residue studies were re-analysed after 30 to 46 months of freezer storage. The total prothioconazole residue data from the 30 to 46-month storage interval were compared with earlier analyses of the same samples conducted after one to three months and 18 to 32 months of freezer storage.

Residues were analysed with a total residue method converting prothioconazole-derived residues to JAU 6476-desthio and JAU 6476-sulfonic acid. The residue components detected were expressed as parent molar equivalents and summed with unchanged JAU 6476-desthio (expressed as parent molar equivalents) to give a total prothioconazole derived residue.

Concurrent recoveries of prothioconazole and JAU6476-desthio from the two and four month intervals are presented in Table 43. Actual recoveries in the storage stability samples were corrected with the concurrent recoveries.

Table 43 Concurrent recoveries of prothioconazole and JAU6476-desthio in plant matrices

Matrix	Storage Interval (days)	Fortification Level (mg/kg)	JAU6476		JAU6476-desthio	
			% Recoveries	% Mean	% Recoveries	% Mean
Wheat Forage	59	0.250	82, 82	82	95, 96	96
	130	0.250	79, 77	78	92, 96	94
Wheat Straw	60	0.250	88, 90	89	91, 90	91
	130	0.250	86, 87	87	90, 91	91
Wheat Grain	61	0.250	90, 91	90	100, 99	99
	131	0.250	86, 87	86	90, 91	91
Wheat Bran	63	0.250	88, 90	89	96, 95	95
	131	0.250	79, 89	84	96, 98	97
Wheat Flour	57	0.250	89, 89	89	99, 97	98
	127	0.250	80, 80	80	94, 95	95
Canola Seed	63	0.250	87, 86	86	96, 93	95
	129	0.250	74, 74	74	95, 95	95
Canola Oil	64	0.250	92, 92	92	99, 99	99
	132	0.250	94, 91	93	93, 93	93
Mustard Greens	58	0.250	88, 88	88	95, 95	95
	127	0.250	90, 87	88	100, 97	99
Tomato Fruit	57	0.250	105, 104	105	95, 95	95
	126	0.250	71, 71	71	92, 94	93
Tomato Paste	58	0.250	89, 85	87	97, 98	98
	126	0.250	89, 89	89	90, 94	92
Turnip Roots	57	0.250	85, 84	84	93, 93	93
	125	0.250	74, 74	74	96, 94	95

The results from a freezer storage stability study (currently in progress) are shown in Table 44 (Thomas JC, Personal communication 2008) After four months of freezer storage, prothioconazole and JAU6476-desthio were both found to be stable (< 30% decomposition) in wheat forage, straw, grain, bran, and flour; canola seed and oil; mustard greens; tomato fruit and paste and turnip roots. Decomposition of prothioconazole and JAU6476-desthio ranged from 0 to 19% and from 0 to 6%, respectively.

Table 44 Summary of freezer storage stability of prothioconazole and JAU6476-desthio residue in plant matrices

Matrix	Storage Interval (days)	Fortification Level (mg/kg)	prothioconazole		JAU6476-desthio	
			% Corr.[a] mean recoveries	Average % Decom-position	% Corr.[a] mean recoveries	Average % Decom-position
Wheat Forage	59	0.250	92	8	101	0
	130	0.250	89	11	96	4
Wheat Straw	60	0.250	95	5	103	0
	130	0.250	87	13	96	4
Wheat Grain	61	0.250	88	12	95	5
	131	0.250	88	12	98	2

Matrix	Storage Interval (days)	Fortification Level (mg/kg)	prothioconazole		JAU6476-desthio	
			% Corr.[a] mean recoveries	Average % Decom-position	% Corr.[a] mean recoveries	Average % Decom-position
Wheat Bran	63	0.250	84	16	103	0
	131	0.250	81	19	95	5
Wheat Flour	57	0.250	98	2	98	2
	127	0.250	102	0	98	2
Canola Seed	63	0.250	95	5	101	0
	129	0.250	89	11	94	6
Canola Oil	64	0.250	96	4	100	0
	132	0.250	92	8	97	3
Mustard Greens	58	0.250	89	11	101	0
	127	0.250	85	15	95	5
Tomato Fruit	57	0.250	88	12	101	0
	126	0.250	87	13	96	4
Tomato Paste	58	0.250	97	3	99	1
	126	0.250	88	12	98	2
Turnip Roots	57	0.250	97	3	99	1
	125	0.250	94	6	97	3

[a] Corrected using concurrent recoveries listed in Table 40.

The total prothioconazole (prothioconazole and JAU6476-desthio) residues found in some of the field residue samples from the JAU6476 field crop residue studies on canola, barley and dried peas after 18 to 32 months and after 30 to 46 months of frozen storage are shown in Table 45. The total prothioconazole residues collected at 30 to 46 months expressed as a percent of the data collected at 18 to 32 months are also presented.

Table 45 Summary of freezer storage stability of total prothioconazole residue in plant matrices

Matrix	Residue found at 18–32 months		Re-analysis of samples		
	Months Stored	Total Residues (mg/kg)	Months Stored	Total Residues (mg/kg)	% of residue [a] found at 18–32 months
Canola					
Seed	28	0.074	41	0.07	95
Seed	28	0.097	41	0.076	78
Barley					
Hay	32	1.814	45	1.777	98
Hay	32	1.741	45	1.621	93
Hay	32	2.577	45	2.361	92
Hay	32	1.668	45	1.676	100
Straw	31	1.336	44	1.615	121
Straw	31	1.321	44	1.514	115
Straw	30	1.324	43	1.36	103

Matrix	Residue found at 18–32 months		Re-analysis of samples		
	Months Stored	Total Residues (mg/kg)	Months Stored	Total Residues (mg/kg)	% of residue [a] found at 18–32 months
Straw	30	1.269	43	1.241	98
Grain	31	0.088	44	0.084	95
Grain	31	0.082	44	0.096	117
Grain	30	0.059	43	0.068	115
Grain	30	0.083	43	0.099	119
Dried Peas					
Peas	18	0.12	30	0.11	92
Peas	18	0.122	30	0.115	94
Peas	18	0.102	30	0.107	105
Peas	18	0.118	30	0.109	92
Wheat					
Forage	30	1.827	45	1.335	73
Forage	30	1.383	45	1.426	103
Forage	30	0.273	45	0.255	93
Forage	30	0.325	45	0.249	77
Hay	30	0.71	45	0.794	112
Hay	30	1.063	45	1.146	108
Hay	30	1.928	44	2.134	111
Hay	30	2.501	44	2.546	102
Straw	30	0.93	44	0.923	99
Straw	30	1.053	44	0.948	90
Straw	29	1.284	44	1.125	88
Straw	29	1.548	44	1.654	107

[a] $\text{Percent value} = \frac{\text{ppm Total JAU6476 Residue Found at 30 to 46 months}}{\text{ppm Total JAU6476 Residue Found at 18 to 32 months}} \times 100$

USE PATTERN

Prothioconazole (JAU 6476) is a systemic fungicide with protective, curative and eradicative abilities. It belongs to the demethylation inhibitor (DMI) fungicide group. It acts by inhibiting the cytochrome P450-dependent C-14 demethylase reaction in fungal sterol biosynthesis. It can be used to control diseases such as eyespot (*Pseudocercosporella herpotrichoides*), Fusarium ear blight (*Fusarium* spp. and *Microdochium nivale*), leaf blotch diseases (*Septoria tritici*, *Leptosphaeria nodorum*, *Pyrenophora* spp. and *Rhynchosporium secalis*, etc.), rust (*Puccinia* spp.), and powdery mildew (*Blumeria graminis*), by foliar application in wheat, barley and other crops. It also can be used as a seed dressing for the control of *Ustilago* spp., *Tilletia* spp., *Fusarium* spp. and *Microdochium nivale*.

Its main metabolite JAU 6476-desthio (M04) belongs chemically also to the group of DMIs. The observed fungicidal activity is caused by the prothioconazole and the metabolite JAU 6476-desthio as an additive effect. The main crops targeted are cereals (barley, oats, wheat, rye, and triticale), pulses (beans and peas), oil seed rape and groundnuts (peanuts). Further commercial uses of prothioconazole exist in ryegrass, spelt, lupins and mustard.

Products containing the active substance prothioconazole are sold under different trade names depending on mixing partners, the type of formulation, the country and market segments.

The use patterns which are supported by residue data are summarized in Tables 46 and 47.

Table 46 Use pattern of prothioconazole for seed dressing with one application

Crop	Country	Trade name Formulation type/ Content (g/L)	Application		PHI (days)
			Rate [a]	Water rate	
Barley	Austria	REDIGO FS100 prothioconazole (100)	100 mg/kg seed	0.2– 0.4 L/dt[a]	n.a
Barley	France	REDIGO FS100 prothioconazole (100)	75 mg/kg seed 13.5 g/ha	0.93– 1.13 L/dt	n.a
Barley	Turkey	LAMARDOR FS 400 prothioconazole + tebuconazole (250 + 150)	37.5 mg/kg seed 7.5 g/ha	0.5–1.5 L/dt	n.a
Barley	United Kingdom	RAXIL PRO FS 050 prothioconazole + tebuconazole + triazoxide (25 + 15 + 10)	50 mg/kg seed 10 g/ha		n.a
Barley. spring	Belarus	LAMARDOR FS 400 prothioconazole + tebuconazole (250 + 150)	37.5–50 mg/kg seed	0.88–1 L/dt	n.a
Barley. spring	Estonia	BARITON FS 075 fluoxastrobin + prothioconazole (37.5 + 37.5)	46.9 mg/kg seed	0.45– 0.85 L/dt	n.a
Barley. spring	Germany	EFA FS 76.25 fluoxastrobin + prothioconazole + tebuconazole + triazoxide (37.5 + 25 + 3.75 + 10)	40 mg/kg seed 7.2 g/ha		n.a
Barley. spring	Kazakhstan	LAMARDOR FS 400 prothioconazole + tebuconazole (250 + 150)	30–37.5 mg/kg seed	0.88–1 L/dt	n.a
Barley. spring	Ukraine	LAMARDOR FS 400 prothioconazole + tebuconazole (250 + 150)	50 mg/kg seed	0.88–1 L/dt	n.a
Barley. winter	Estonia	BARITON FS 075 fluoxastrobin + prothioconazole (37.5 + 37.5)	56.2 mg/kg seed	0.45– 0.85 L/dt	n.a
Barley. winter	Germany	EFA FS 76.25 fluoxastrobin + prothioconazole + tebuconazole + triazoxide (37.5 + 25 + 3.75 + 10)	40 mg/kg seed 7.2 g/ha		n.a
Barley. winter	Slovakia	SCENIC FS 080 fluoxastrobin + prothioconazole + tebuconazole (37.5 + 37.5 + 5)	37.5 mg/kg seed 9.4 g/ha	0.88–1 L/dt	n.a
Barley. winter	United Kingdom	RAXIL DETER FS 399.9 clothianidin + prothioconazole + tebuconazole + triazoxide (333.3 + 33.3 + 20 + 13.3)	50 mg/kg seed 10 g/ha		n.a
Barley. winter	United Kingdom	REDIGO FS 100 prothioconazole (100)	100 mg/kg seed 18 g/ha		n.a
Barley. winter	United Kingdom	REDIGO DETER FS 300 clothianidin + prothioconazole (250 + 50)	100 mg/kg seed 20 g/ha		n.a

Crop	Country	Trade name Formulation type/ Content (g/L)	Application		PHI (days)
			Rate [a]	Water rate	
Oats	Estonia	BARITON FS 075 fluoxastrobin + prothioconazole (37.5 + 37.5)	46.9 mg/kg seed	0.45– 0.85 L/dt	n.a
Oats	France	REDIGO FS100 prothioconazole (100)	100 mg/kg seed 18 g/ha	0.9–1.1 L/dt	n.a
Oats	Germany	EFA FS 76.25 fluoxastrobin + prothioconazole + tebuconazole + triazoxide (37.5 + 25 + 3.75 + 10)	25 mg/kg seed 4.2 g/ha		n.a
Oats. winter	United Kingdom	REDIGO DETER FS 300 clothianidin + prothioconazole (250 + 50)	100 mg/kg seed 16 g/ha		n.a
Oats	United Kingdom	REDIGO FS 100 prothioconazole (100)	100 mg/kg seed 18 g/ha		n.a
Oats	United Kingdom	REDIGO TWIN FS 075 fluoxastrobin + prothioconazole (37.5 + 37.5)	56.2 mg/kg seed 12.9 g/ha		n.a
Rye	Austria	REDIGO FS 100 prothioconazole (100)	100 mg/kg seed	0.2–0.4 L/dt	n.a
Rye	Czech Republic	SCENIC FS 080 fluoxastrobin + prothioconazole + tebuconazole (37,5 + 37,5 + 5)	37.5 mg/kg seed 7.5 g/ha	0.5 L/dt	n.a
Rye	France	REDIGO FS 100 prothioconazole (100)	100 mg/kg seed 18 g/ha	0.9–1.1 L/dt	n.a
Rye	Germany	BAYAZZO FS 080 fluoxastrobin + prothioconazole + tebuconazole (37,5 + 37,5 + 5)	45 mg/kg seed 7.2 g/ha		n.a
Rye	Germany	EFA FS 76,25 fluoxastrobin + prothioconazole + tebuconazole +triazoxide (37,5 + 25 + 3,75 + 10)	30 mg/kg seed 4.8 g/ha		n.a
Rye	Germany	TOLEDO FS 075 fluoxastrobin + prothioconazole (37,5 + 37,5)	45 mg/kg seed 7.2 g/ha		n.a
Rye	Latvia	BARITON FS 075 fluoxastrobin + prothioconazole (37,5 + 37,5)	56.2 mg/kg seed	0.45– 0.85 L/dt	n.a
Rye	Poland	SCENIC FS 080 fluoxastrobin + prothioconazole + tebuconazole (37,5 + 37,5 + 5)	7.5 g/ha	400– 800 L/ha	n.a
Rye	Slovakia	SCENIC FS 080 fluoxastrobin + prothioconazole + tebuconazole (37,5 + 37,5 + 5)	37.5 mg/kg seed 9.4 g/ha		n.a
Rye	Switzerland	SCENIC FS 080 fluoxastrobin + prothioconazole + tebuconazole (37,5 + 37,5 + 5)	56.2 mg/kg seed 9.0 g/ha		n.a
Rye	United Kingdom	REDIGO FS 100 prothioconazole (100)	100 mg/kg seed 18 g/ha		n.a

Crop	Country	Trade name Formulation type/ Content (g/L)	Application		PHI (days)
			Rate [a]	Water rate	
Rye	United Kingdom	REDIGO DETER FS 300 clothianidin + prothioconazole (250 + 50)	100 mg/kg seed 16 g/ha		n.a
Rye	United Kingdom	REDIGO TWIN FS 075 fluoxastrobin + prothioconazole (37,5 + 37,5)	56.2 mg/kg seed 12.9 g/ha		n.a
Rye, winter	Estonia	BARITON FS 075 fluoxastrobin + prothioconazole (37,5 + 37,5)	56.2 mg/kg seed	0.45– 0.85 L/dt	n.a
Triticale	Austria	REDIGO FS 100 prothioconazole (100)	100 mg/kg seed	0.2–0.4 L/dt	n.a
Triticale	Czech Republic	SCENIC FS 080 fluoxastrobin + prothioconazole + tebuconazole (37,5 + 37,5 + 5)	37.5 mg/kg seed 7.5 g/ha	0.5 L/dt	n.a
Triticale	Estonia	BARITON FS 075 fluoxastrobin + prothioconazole (37,5 + 37,5)	56.2 mg/kg seed	0.45– 0.85 L/dt	n.a
Triticale	France	REDIGO FS 100 prothioconazole (100)	100 mg/kg seed 18 g/ha	0.9–1.1 L/dt	n.a
Triticale	Germany	BAYAZZO FS 080 fluoxastrobin + prothioconazole + tebuconazole (37,5 + 37,5 + 5)	45 mg/kg seed 7.2 g/ha		n.a
Triticale	Germany	EFA FS 76,25 fluoxastrobin + prothioconazole + tebuconazole +triazoxide (37,5 + 25 + 3,75 + 10)	30 mg/kg seed 4.8 g/ha		n.a
Triticale	Germany	TOLEDO FS 075 fluoxastrobin + prothioconazole (37,5 + 37,5)	56.2 mg/kg seed 9.0 g/ha		n.a
Triticale	Latvia	BARITON FS 075 fluoxastrobin + prothioconazole (37,5 + 37,5)	56.2 mg/kg seed	0.45– 0.85 L/dt	n.a
Triticale	Poland	SCENIC FS 080 fluoxastrobin + prothioconazole + tebuconazole (37,5 + 37,5 + 5)	7.5 g/ha	400– 800 L/ha	n.a
Triticale	Slovakia	SCENIC FS 080 fluoxastrobin + prothioconazole + tebuconazole (37,5 + 37,5 + 5)	37.5 mg/kg seed 9.4 g/ha		n.a
Triticale	Switzerland	SCENIC FS 080 fluoxastrobin + prothioconazole + tebuconazole (37,5 + 37,5 + 5)	56.2 mg/kg seed 9.0 g/ha		n.a
Triticale	United Kingdom	REDIGO FS 100 prothioconazole (100)	100 mg/kg seed 18 g/ha		n.a
Triticale	United Kingdom	REDIGO DETER FS 300 clothianidin + prothioconazole (250 + 50)	100 mg/kg seed 16 g/ha		n.a
Triticale	United Kingdom	REDIGO TWIN FS 075 fluoxastrobin + prothioconazole (37,5 + 37,5)	56.2 mg/kg seed 12.9 g/ha		n.a

Crop	Country	Trade name Formulation type/ Content (g/L)	Application		PHI (days)
			Rate [a]	Water rate	
Wheat	Argentina	PUCARA FS 400 prothioconazole + tebuconazole (250 + 150)	50 mg/kg seed 0.55 g/ha	1–1.5 L/dt	n.a
Wheat	Austria	REDIGO FS 100 prothioconazole (100)	100 mg/kg seed	0.2–0,4 L/dt	n.a
Wheat, winter	Belarus	LAMARDOR FS 400 prothioconazole + tebuconazole (250 + 150)	50 mg/kg seed	0.88–1 L/dt	n.a
Wheat	Czech Republic	SCENIC FS 080 fluoxastrobin + prothioconazole + tebuconazole (37,5 + 37,5 + 5)	37.5 mg/kg seed 9.4 g/ha	0.5 L/dt	n.a
Wheat	Estonia	BARITON FS 075 fluoxastrobin + prothioconazole (37,5 + 37,5)	46.9 mg/kg seed	0.45– 0.85 L/dt	n.a
Wheat	France	REDIGO FS 100 prothioconazole (100)	100 mg/kg seed 18 g/ha	0.9–1.1 L/dt	n.a
Wheat	Germany	BAYAZZO FS 080 fluoxastrobin + prothioconazole + tebuconazole (37,5 + 37,5 + 5)	45 mg/kg seed 7.2 g/ha		n.a
Wheat	Germany	EFA FS 76,25 fluoxastrobin + prothioconazole + tebuconazole +triazoxide (37,5 + 25 + 3,75 + 10)	40 mg/kg seed 9.6 g/ha		n.a
Wheat	Germany	TOLEDO FS 075 fluoxastrobin + prothioconazole (37,5 + 37,5)	60 mg/kg seed 14.4 g/ha		n.a
Wheat, spring	Kazakhstan	LAMARDOR FS 400 prothioconazole + tebuconazole (250 + 150)	37.5 mg/kg seed	0.8–1 L/dt	n.a
Wheat, winter	Latvia	BARITON FS 075 fluoxastrobin + prothioconazole (37,5 + 37,5)	56.2 mg/kg seed	0.45– 0.85 L/dt	n.a
Wheat, winter	Lithuania	BARITON FS 075 fluoxastrobin + prothioconazole (37,5 + 37,5)	56.2 mg/kg seed	0.45– 0.85 L/dt	n.a
Wheat	Poland	SCENIC FS 080 fluoxastrobin + prothioconazole + tebuconazole (37,5 + 37,5 + 5)	7.5 g/ha	400– 800 L/ha	n.a
Wheat	Saudi Arabia	LAMARDOR FS 400 prothioconazole + tebuconazole (250 + 150)	37.5 mg/kg seed 7.5 g/ha	1.2–1.6 L/dt	n.a
Wheat	Slovakia	SCENIC FS 080 fluoxastrobin + prothioconazole + tebuconazole (37,5 + 37,5 + 5)	37.5 mg/kg seed 9.4 g/ha		n.a
Wheat	Switzerland	SCENIC FS 080 fluoxastrobin + prothioconazole + tebuconazole (37,5 + 37,5 + 5)	75 mg/kg seed 18 g/ha		n.a

Crop	Country	Trade name Formulation type/ Content (g/L)	Application		PHI (days)
			Rate [a]	Water rate	
Wheat, winter	Turkey	LAMARDOR FS 400 prothioconazole + tebuconazole (250 + 150)	37.5 mg/kg seed 7.5 g/ha	0.5–1.5 L/dt	n.a
Wheat, winter	Ukraine	LAMARDOR FS 400 prothioconazole + tebuconazole (250 + 150)	50 mg/kg seed	0.88–1 L/dt	n.a
Wheat	United Kingdom	REDIGO FS 100 prothioconazole (100)	100 mg/kg seed 18 g/ha		n.a
Wheat	United Kingdom	REDIGO DETER FS 300 clothianidin + prothioconazole (250 + 50)	100 mg/kg seed 16 g/ha		n.a
Wheat	United Kingdom	REDIGO TWIN FS 075 fluoxastrobin + prothioconazole (37,5 + 37,5)	56.2 mg/kg seed 12.9 g/ha	0.2–0.4 L/dt	n.a
Wheat, winter	United Kingdom	SCENIC FS 080 fluoxastrobin + prothioconazole + tebuconazole (37,5 + 37,5 + 5)	56.2 mg/kg seed 12.9 g/ha		n.a
Wheat, winter	Uzbekistan	LAMARDOR FS 400 prothioconazole + tebuconazole (250 + 150)	37.5 mg/kg seed	0.88–1 L/dt	n.a

dt = 100 kg (of seed);

n.a.: not applicable

Table 47 Use pattern of prothioconazole for foliar application with spraying in cereals

Crop	Country	Trade name Formulation type/ Content (g/L)	Application			PHI (days)
			Rate	Water	No.	
Barley	Belgium	FANDANGO EC 200 fluoxastrobin + prothioconazole (100 + 100)	125 g/ha	150–300 L/ha	2	BBCH49
Barley	Belgium	INPUT PRO EC 250 Prothioconazole (250)	125 g/ha		2	n.a
Barley	Denmark	PROLINE EC 250 prothioconazole (250)	175 g/ha	150–300 L/ha	2	45 BBCH69
Barley	Denmark	PROLINE EC 250 prothioconazole (250)	175 g/ha	150–300 L/ha	2	45 BBCH69
Barley	Estonia	FANDANGO EC 200 fluoxastrobin + prothioconazole (100 + 100)	100 g/ha	200–400 L/ha	2	BBCH61
Barley	Estonia	INPUT EC 460 prothioconazole + spiroxamine (160 + 300)	160 g/ha	200–400 L/ha	2	n.a
Barley	Estonia	PROSARO EC 250 prothioconazole + tebuconazole (125 + 125)	125 g/ha	200–300 L/ha	2	35 BBCH61

Crop	Country	Trade name Formulation type/ Content (g/L)	Application			PHI (days)
			Rate	Water	No.	
Barley	Finland	PROLINE EC 250 prothioconazole (250)	175 g/ha	150–300 L/ha	2	45 BBCH69
Barley	France	FANDANGO S EC 150 fluoxastrobin + prothioconazole (50 + 100)	175 g/ha	100–400 L/ha	2	35
Barley	France	JOAO EC 250 prothioconazole (250)	200 g/ha	100–400 L/ha	2	35
Barley	Germany	FANDANGO EC 200 fluoxastrobin + prothioconazole (100 + 100)	125 g/ha		2	n.a
Barley,	Germany	INPUT EC 460 prothioconazole + spiroxamine (160 + 300)	200 g/ha	200–400 L/ha	2	n.a
Barley	Germany	PROLINE EC 250 prothioconazole (250)	200 g/ha		2	49
Barley	Ireland	CELLO EC 450 prothioconazole + spiroxamine + tebuconazole (100 + 250 + 100)	125 g/ha	200–300 L/ha	2	BBCH59
Barley	Ireland	COYOTE EC 300 fluoxastrobin + prothioconazole + trifloxystrobin (75 + 150 + 75)	120 g/ha	200–300 L/ha	2	BBCH61
Barley	Ireland	FANDANGO EC 200 fluoxastrobin + prothioconazole (100 + 100)	125 /ha	200–300 L/ha	2	BBCH61
Barley	Ireland	HELIX EC 460 prothioconazole + spiroxamine (160 + 300)	200 g/ha	200–300 L/ha	2	BBCH59
Barley	Ireland	METTLE EC 200 fluoxastrobin + prothioconazole (100 + 100)	125 g/ha	200–300 L/ha	2	BBCH59
Barley	Ireland	PROLINE EC 250 prothioconazole (250)	200 g/ha		2	BBCH61
Barley	Ireland	PROSARO EC 250 prothioconazole + tebuconazole (125 + 125)	150 g/ha	200–300 L/ha	2	BBCH61

Crop	Country	Trade name Formulation type/ Content (g/L)	Application			PHI (days)
			Rate	Water	No.	
Barley	Ireland	ZEPHYR SC 263 prothioconazole + trifloxystrobin (175 + 88)	131 g/ha	200–300 L/ha	2	n.a
Barley	Latvia	FANDANGO EC 200 fluoxastrobin + prothioconazole (100 + 100)	100 g/ha	200–400 L/ha	2	35 BBCH61
Barley	Latvia	INPUT EC 460 prothioconazole + spiroxamine (160 + 300)	160 g/ha	200–400 L/ha	2	42
Barley	Latvia	PROSARO EC 250 prothioconazole + tebuconazole (125 + 125)	125 g/ha	200–300 L/ha	2	35
Barley	Lithuania	FANDANGO EC 200 fluoxastrobin + prothioconazole (100 + 100)	100 g/ha	200–400 L/ha	2	35 BBCH61
Barley	Lithuania	INPUT EC 460 prothioconazole + spiroxamine (160 + 300)	160 g/ha	200–400 L/ha	2	35
Barley	Lithuania	PROSARO EC 250 prothioconazole + tebuconazole (125 + 125)	125 g/ha	200–300 L/ha	2	35
Barley	Luxembourg	FANDANGO EC 200 fluoxastrobin + prothioconazole (100 + 100)	125 g/ha	150–300 L/ha	2	BBCH49
Barley	Netherlands	FANDANGO EC 200 fluoxastrobin + prothioconazole (100 + 100)	125 g/ha	200–600 L/ha	2	n.a
Barley	Netherlands	PROLINE EC 250 prothioconazole (250)	200 g/ha	200–600 L/ha	2	n.a
Barley	New Zealand	FANDANGO EC 200 fluoxastrobin + prothioconazole (100 + 100)	150 g/ha	200 L/ha	2	56
Barley	New Zealand	PROLINE EC 250 prothioconazole (250)	200 g/ha	50–200 L/ha	2	56
Barley	Slovakia	PROSARO EC 250 prothioconazole + tebuconazole (125 + 125)	100 g/ha	400 L/ha	1	n.a

Crop	Country	Trade name Formulation type/ Content (g/L)	Application			PHI (days)
			Rate	Water	No.	
Barley	Switzerland	INPUT EC 460 prothioconazole + spiroxamine (160 + 300)	200 g/ha	300–500 L/ha	1	n.a
Barley	Switzerland	PROLINE EC 250 prothioconazole (250)	200 g/ha		1	BBCH51
Barley	Switzerland	PROSARO EC 250 prothioconazole + tebuconazole (125 + 125)	125 g/ha		1	BBCH51
Barley	United Kingdom	CELLO EC 450 prothioconazole + spiroxamine + tebuconazole (100 + 250 + 100)	125 g/ha	200–400 L/ha	2	BBCH61
Barley	United Kingdom	FANDANGO EC 200 fluoxastrobin + prothioconazole (100 + 100)	125 g/ha	200–300 L/ha	2	BBCH61
Barley	United Kingdom	HELIX EC 460 prothioconazole + spiroxamine (160 + 300)	200 g/ha	200–300 L/ha	2	BBCH61
Barley	United Kingdom	JAUNT EC 300 fluoxastrobin + prothioconazole + trifloxystrobin (75 + 150 + 75)	120 g/ha		2	BBCH61
Barley	United Kingdom	MAESTRO EC 200 fluoxastrobin + prothioconazole (100 + 100)	125 g/ha	200–300 L/ha	2	BBCH61
Barley	United Kingdom	MAESTRO EC 200 fluoxastrobin + prothioconazole (100 + 100)	125 g/ha	200–300 L/ha	2	BBCH61
Barley	United Kingdom	MOBIUS SC 325 prothioconazole + trifloxystrobin (175 + 150)	131 g/ha		2	BBCH61
Barley	United Kingdom	PROLINE EC 250 prothioconazole (250)	200 g/ha		2	n.a
Barley	United Kingdom	MOBIUS SC 325 prothioconazole + trifloxystrobin (175 + 150)	131 g/ha		2	BBCH61
Barley	United Kingdom	PROSARO EC 250 prothioconazole + tebuconazole (125 + 125)	150 g/ha	200–300 L/ha	2	BBCH61

Crop	Country	Trade name Formulation type/ Content (g/L)	Application			PHI (days)
			Rate	Water	No.	
Barley	United Kingdom	ZEPHYR SC 263 prothioconazole + trifloxystrobin (175 + 88)	131 g/ha		2	BBCH61
Barley	United States	PROLINE SC 480 prothioconazole (480)	150 g/ha		2	32
Barley	United States	PROLINE SC 480 prothioconazole (480)	200 g/ha		1	32
Barley, spring	Czech Republic	FANDANGO EC 200 fluoxastrobin + prothioconazole (100 + 100)	120 g/ha	200–400 L/ha	2	35
Barley, spring	Czech Republic	PROLINE EC 250 prothioconazole (250)	200 g/ha	200–400 L/ha	2	35
Barley, spring	Czech Republic	PROSARO EC 250 prothioconazole + tebuconazole (125 + 125)	125 g/ha	200–400 L/ha	2	35
Barley, spring	Luxembourg	INPUT PRO EC 250 prothioconazole (250)	200 g/ha		2	n.a
Barley, spring	Poland	FANDANGO EC 200 fluoxastrobin + prothioconazole (100 + 100)	100 g/ha	200–400 L/ha	1	n.a
Barley, spring	Poland	PROSARO EC 250 prothioconazole + tebuconazole (125 + 125)	125 g/ha	200–400 L/ha	1	35
Barley, spring	Slovakia	FANDANGO EC 200 fluoxastrobin + prothioconazole (100 + 100)	100 g/ha	400 L/ha	1	n.a
Barley, spring	Slovakia	PROLINE EC 250 prothioconazole (250)	200 g/ha	400 L/ha	1	n.a
Barley, spring	Sweden	PROLINE EC 250 prothioconazole (250)	175 g/ha	150–300 L/ha	2	45 BBCH69
Oats	Estonia	PROSARO EC 250 prothioconazole + tebuconazole (125 + 125)	125 g/ha	200–300 L/ha	2	35 BBCH61
Oats	France	FANDANGO S EC 150 fluoxastrobin + prothioconazole (50 + 100)	200 g/ha	100–400 L/ha	2	35
Oats	France	JOAO EC 250 prothioconazole (250)	200 g/ha	100–400 L/ha	2	35
Oats	Ireland	CELLO EC 450 prothioconazole + spiroxamine + tebuconazole (100 + 250 + 100)	125 g/ha	200–300 L/ha	2	BBCH59

Crop	Country	Trade name Formulation type/ Content (g/L)	Application			PHI (days)
			Rate	Water	No.	
Oats	Ireland	FANDANGO EC 200 fluoxastrobin + prothioconazole (100 + 100)	125 g/ha	200–300 L/ha	2	n.a
Oats	Ireland	HELIX EC 460 prothioconazole + spiroxamine (160 + 300)	200 g/ha	200–300 L/ha	2	BBCH59
Oats	Ireland	METTLE EC 200 fluoxastrobin + prothioconazole (100 + 100)	125 g/ha	200–300 L/ha	2	BBCH61
Oats	Ireland	PROLINE EC 250 prothioconazole (250)	200 g/ha		2	n.a
Oats	Ireland	PROSARO EC 250 prothioconazole + tebuconazole (125 + 125)	125 g/ha		2	BBCH61
Oats	Latvia	PROSARO EC 250 prothioconazole + tebuconazole (125 + 125)	125 g/ha	200–300 L/ha	2	35
Oats	United Kingdom	CELLO EC 450 prothioconazole + spiroxamine + tebuconazole (100 + 250 + 100)	125 g/ha	200–400 L/ha	2	BBCH61
Oats	United Kingdom	FANDANGO EC 200 fluoxastrobin + prothioconazole (100 + 100)	125 g/ha	200–400 L/ha	2	n.a
Oats	United Kingdom	HELIX EC 460 prothioconazole + spiroxamine (160 + 300)	200 g/ha	200–400 L/ha	2	BBCH61
Oats	United Kingdom	MAESTRO EC 200 fluoxastrobin + prothioconazole (100 + 100)	125 g/ha		2	BBCH61
Oats	United Kingdom	PROLINE EC 250 prothioconazole (250)	200 g/ha	200–400 L/ha	2	n.a
Oats	United Kingdom	PROSARO EC 250 prothioconazole + tebuconazole (125 + 125)	125 g/ha	200–400 L/ha	2	n.a
Oats, winter	Belgium	PROSARO EC 250 prothioconazole + tebuconazole (125 + 125)	125 g/ha		1	n.a

Crop	Country	Trade name Formulation type/ Content (g/L)	Application			PHI (days)
			Rate	Water	No.	
Oats, winter	Luxembourg	PROSARO EC 250 prothioconazole + tebuconazole (125 + 125)	125 g/ha		1	n.a
Rye	Belgium	FANDANGO EC 200 fluoxastrobin + prothioconazole (100 + 100)	150 g/ha	150–300 L/ha	2	BBCH59
Rye	Belgium	INPUT PRO EC 250 Prothioconazole (250)	200 g/ha		2	35
Rye	Belgium	PROSARO EC 250 prothioconazole + tebuconazole (125 + 125)	125 g/ha		1	n.a
Rye	Czech Republic	PROSARO EC 250 prothioconazole + tebuconazole (125 + 125)	150 g/ha	200–400 L/ha	2	35
Rye	Czech Republic	PROLIN EC 250 prothioconazole (250)	200 g/ha	200–400 L/ha	2	35
Rye	Denmark	PROLINE EC 250 prothioconazole (250)	150 g/ha	150–300 L/ha	2	35
Rye	Estonia	INPUT EC 460 prothioconazole + spiroxamine (160 + 300)	160 g/ha	200–400 L/ha	2	n.a
Rye	Estonia	PROSARO EC 250 prothioconazole + tebuconazole (125 + 125)	125 g/ha	200–300 L/ha	2	35
Rye	Finland	PROLINE EC 250 prothioconazole (250)	150 g/ha	150–300 L/ha	2	35
Rye	France	FANDANGO S EC 150 fluoxastrobin + prothioconazole (50 + 100)	200 g/ha	100–400 L/ha	2	35
Rye	France	JOAO EC 250 prothioconazole (250)	200 g/ha	100–400 L/ha	2	35
Rye	Germany	FANDANGO EC 200 fluoxastrobin + prothioconazole (100 + 100)	150 g/ha		2	n.a
Rye	Germany	INPUT EC 460 prothioconazole + spiroxamine (160 + 300)	200 g/ha	200–400 L/ha	2	n.a
Rye	Germany	PROLINE EC 250 prothioconazole (250)	200 g/ha		3	35

Crop	Country	Trade name Formulation type/ Content (g/L)	Application			PHI (days)
			Rate	Water	No.	
Rye	Latvia	INPUT EC 460 prothioconazole + spiroxamine (160 + 300)	160 g/ha	200–400 L/ha	2	42
Rye	Latvia	PROSARO EC 250 prothioconazole + tebuconazole (125 + 125)	125 g/ha	200–300 L/ha	2	35
Rye	Luxembourg	FANDANGO EC 200 fluoxastrobin + prothioconazole (100 + 100)	150 g/ha	150–300 L/ha	2	n.a
Rye	Luxembourg	INPUT PRO EC 250 prothioconazole (250)	200 g/ha		2	n.a
Rye	Luxembourg	PROSARO EC 250 prothioconazole + tebuconazole (125 + 125)	125 g/ha	200–300 L/ha	1	n.a
Rye	Sweden	PROLINE EC 250 prothioconazole (250)	150 g/ha	150–300 L/ha	2	35
Rye	Switzerland	INPUT EC 460 prothioconazole + spiroxamine (160 + 300)	200 g/ha	300–500 L/ha	1	n.a
Rye	Switzerland	PROLINE EC 250 prothioconazole (250)	200 g/ha		1	BBCH61
Rye	Switzerland	PROSARO EC 250 prothioconazole + tebuconazole (125 + 125)	125 g/ha		1	BBCH61
Rye, winter	Estonia	FANDANGO EC 200 fluoxastrobin + prothioconazole (100 + 100)	100 g/ha	200–400 L/ha	2	BBCH69
Rye, winter	Ireland	CELLO EC 450 prothioconazole + spiroxamine + tebuconazole (100 + 250 + 100)	125 g/ha	200–300 L/ha	2	BBCH71
Rye, winter	Ireland	FANDANGO EC 200 fluoxastrobin + prothioconazole (100 + 100)	150 g/ha	200–300 L/ha	2	BBCH71
Rye, winter	Ireland	HELIX EC 460 prothioconazole + spiroxamine (160 + 300)	200 g/ha	200–300 L/ha	3	BBCH71
Rye, winter	Ireland	METTLE EC 200 fluoxastrobin + prothioconazole (100 + 100)	150 g/ha	200–300 L/ha	2	BBCH71
Rye, winter	Ireland	PROLINE EC 250 prothioconazole (250)	200 g/ha		3	BBCH71

Crop	Country	Trade name Formulation type/ Content (g/L)	Application			PHI (days)
			Rate	Water	No.	
Rye, winter	Ireland	PROSARO EC 250 prothioconazole + tebuconazole (125 + 125)	150 g/ha	200–300 L/ha	3	BBCH71
Rye, winter	Latvia	FANDANGO EC 200 fluoxastrobin + prothioconazole (100 + 100)	100 g/ha	200–400 L/ha	2	35 BBCH69
Rye, winter	Lithuania	FANDANGO EC 200 fluoxastrobin + prothioconazole (100 + 100)	100 g/ha	200–400 L/ha	2	35 BBCH69
Rye, winter	Netherlands	PROLINE EC 250 prothioconazole 250)	200 g/ha	200–400 L/ha	2	n.a
Rye, winter	United Kingdom	CELLO EC 450 prothioconazole + spiroxamine + tebuconazole (100 + 250 + 100)	125 g/ha	200–400 L/ha	2	BBCH71
Rye, winter	United Kingdom	FANDANGO EC 200 fluoxastrobin + prothioconazole (100 + 100)	150 g/ha	200–300 L/ha	2	BBCH71
Rye, winter	United Kingdom	HELIX EC 460 prothioconazole + spiroxamine (160 + 300)	200 g/ha	200–300 L/ha	3	BBCH71
Rye, winter	United Kingdom	MAESTRO EC 200 fluoxastrobin + prothioconazole (100 + 100)	150 g/ha	200–300 L/ha	2	BBCH71
Rye, winter	United Kingdom	PROLINE EC 250 prothioconazole (250)	200 g/ha		3	n.a
Rye, winter	United Kingdom	PROSARO EC 250 prothioconazole + tebuconazole (125 + 125)	150 g/ha	200–300 L/ha	3	BBCH71
Spelt	Belgium	FANDANGO EC 200 fluoxastrobin + prothioconazole (100 + 100)	150 g/ha	150–300 L/ha	2	BBCH65
Spelt	Belgium	PROSARO EC 250 prothioconazole + tebuconazole (125 + 125)	125 g/ha		1	n.a
Spelt	Luxembourg	FANDANGO EC 200 fluoxastrobin + prothioconazole (100 + 100)	150 g/ha	150–300 L/ha	2	BBCH65

Crop	Country	Trade name Formulation type/ Content (g/L)	Application			PHI (days)
			Rate	Water	No.	
Spelt	Luxembourg	PROSARO EC 250 prothioconazole + tebuconazole (125 + 125)	125 g/ha		1	n.a
Triticale	Belgium	FANDANGO EC 200 fluoxastrobin + prothioconazole (100 + 100)	120 g/ha	200–400 L/ha	2	35
Triticale	Belgium	PROSARO EC 250 prothioconazole + tebuconazole (125 + 125)	125 g/ha		1	n.a
Triticale	Czech Republic	PROLINE EC 250 prothioconazole (250)	200 g/ha	200–400 L/ha	2	35
Triticale	Denmark	PROLINE EC 250 prothioconazole (250)	150 g/ha	150–300 L/ha	2	35 BBCH69
Triticale	Estonia	FANDANGO EC 200 fluoxastrobin + prothioconazole (100 + 100)	100 g/ha	200–400 L/ha	2	BBCH69
Triticale	Estonia	INPUT EC 460 prothioconazole + spiroxamine (160 + 300)	160 g/ha	200–400 L/ha	2	Triticale
Triticale	Estonia	PROSARO EC 250 prothioconazole + tebuconazole (125 + 125)	125 g/ha	200–300 L/ha	2	35 BBCH69
Triticale	Finland	PROLINE EC 250 prothioconazole (250)	150 g/ha	150–300 L/ha	2	35 BBCH69
Triticale	France	FANDANGO S EC 150 fluoxastrobin + prothioconazole (50 + 100)	200 g/ha	100–400 L/ha	2	35
Triticale	France	JOAO EC 250 prothioconazole (250)	200 g/ha	100–400 L/ha	2	35
Triticale	Germany	FANDANGO EC 200 fluoxastrobin + prothioconazole (100 + 100)	150 g/ha		2	n.a
Triticale	Germany	INPUT EC 460 prothioconazole + spiroxamine (160 + 300)	200 g/ha	200–400 L/ha	2	n.a
Triticale	Germany	PROLINE EC 250 prothioconazole (250)	200 g/ha		2	35
Triticale	Latvia	FANDANGO EC 200 fluoxastrobin + prothioconazole (100 + 100)	100 g/ha	200–400 L/ha	2	35
Triticale	Latvia	INPUT EC 460 prothioconazole + spiroxamine (160 + 300)	160 g/ha	200–400 L/ha	2	42

Crop	Country	Trade name Formulation type/ Content (g/L)	Application			PHI (days)
			Rate	Water	No.	
Triticale	Latvia	PROSARO EC 250 prothioconazole + tebuconazole (125 + 125)	125 g/ha	200–300 L/ha	2	35
Triticale	Lithuania	PROSARO EC 250 prothioconazole + tebuconazole (125 + 125)	125 g/ha	200–300 L/ha	2	35
Triticale	Luxembourg	PROSARO EC 250 prothioconazole + tebuconazole (125 + 125)	125 g/ha		1	n.a
Triticale	Netherlands	FANDANGO EC 200 fluoxastrobin + prothioconazole (100 + 100)	150 g/ha	200–600 L/ha	2	n.a
Triticale	Sweden	PROLINE EC 250 prothioconazole (250)	150 g/ha	150–300 L/ha	2	35 BBCH69
Triticale	Sweden	PROLINE EC 250 prothioconazole (250)	150 g/ha	150–300 L/ha	2	35 BBCH69
Triticale	Switzerland	INPUT EC 460 prothioconazole + spiroxamine (160 + 300)	200 g/ha	300–500 L/ha	1	n.a
Triticale	Switzerland	PROLINE EC 250 prothioconazole (250)	200 g/ha		1	BBCH61
Triticale	Switzerland	PROSARO EC 250 prothioconazole + tebuconazole (125 + 125)	125 g/ha		1	BBCH61
Wheat	Czech Republic	PROSARO EC 250 prothioconazole + tebuconazole (125 + 125)	93.8 g/ha	200–400 L/ha	2	35
Wheat	Denmark	PROLINE EC 250 prothioconazole (250)	200 g/ha	100–300 L/ha	2	35 BBCH69
Wheat	Estonia	FANDANGO EC 200 fluoxastrobin + prothioconazole (100 + 100)	100 g/ha	200–400 L/ha	2	BBCH69
Wheat	Estonia	INPUT EC 460 prothioconazole + spiroxamine (160 + 300)	160 g/ha	200–400 L/ha	2	n.a
Wheat	Estonia	PROSARO EC 250 prothioconazole + tebuconazole (125 + 125)	125 g/ha	200–300 L/ha	2	35 BBCH69
Wheat	Finland	PROLINE EC 250 prothioconazole (250)	200 g/ha	100–300 L/ha	2	35 BBCH69
Wheat	France	FANDANGO S EC 150 fluoxastrobin + prothioconazole (50 + 100)	200 g/ha	100–400 L/ha	2	35
Wheat	France	JOAO EC 250 prothioconazole (250)	200 g/ha	100–400 L/ha	2	35

Crop	Country	Trade name Formulation type/ Content (g/L)	Application			PHI (days)
			Rate	Water	No.	
Wheat	Germany	FANDANGO EC 200 fluoxastrobin + prothioconazole (100 + 100)	150 g/ha		2	n.a
Wheat	Germany	INPUT EC 460 prothioconazole + spiroxamine (160 + 300)	200 g/ha	200–400 L/ha	2	n.a
Wheat	Germany	PROLINE EC 250 prothioconazole (250)	200 g/ha		3	35
Wheat	Latvia	FANDANGO EC 200 fluoxastrobin + prothioconazole (100 + 100)	100 g/ha	200–400 L/ha	2	35
Wheat	Latvia	INPUT EC 460 prothioconazole + spiroxamine (160 + 300)	160 g/ha	200–400 L/ha	2	42
Wheat	Latvia	PROSARO EC 250 prothioconazole + tebuconazole (125 + 125)	125 g/ha	200–300 L/ha	2	35
Wheat	Lithuania	FANDANGO EC 200 fluoxastrobin + prothioconazole (100 + 100)	100 g/ha	200–400 L/ha	2	35 BBCH69
Wheat	Lithuania	INPUT EC 460 prothioconazole + spiroxamine (160 + 300)	160 g/ha	200–400 L/ha	2	35
Wheat	Lithuania	PROSARO EC 250 prothioconazole + tebuconazole (125 + 125)	125 g/ha	200–300 L/ha	2	35
Wheat	Luxembourg	PROSARO EC 250 prothioconazole + tebuconazole (125 + 125)	125 g/ha	200–300 L/ha	1	n.a
Wheat	Netherlands	FANDANGO EC 200 fluoxastrobin + prothioconazole (100 + 100)	150 g/ha	200–600 L/ha	2	n.a
Wheat	Netherlands	PROLINE EC 250 prothioconazole (250)	200 g/ha	200–600 L/ha	2	n.a
Wheat	New Zealand	FANDANGO EC 200 fluoxastrobin + prothioconazole (100 + 100)	150 g/ha	200 L/ha	2	56
Wheat	New Zealand	PROLINE EC 250 prothioconazole (250)	200 g/ha	50–200 L/ha	3	56
Wheat	Slovakia	PROSARO EC 250 prothioconazole + tebuconazole (125 + 125)	100 g/ha	400 L/ha	1	n.a
Wheat	Sweden	PROLINE EC 250 prothioconazole (250)	200 g/ha	100–300 L/ha	2	35 BBCH69

Crop	Country	Trade name Formulation type/ Content (g/L)	Application			PHI (days)
			Rate	Water	No.	
Wheat	Switzerland	INPUT EC 460 prothioconazole + spiroxamine (160 + 300)	200 g/ha	300–500 L/ha	1	n.a
Wheat	Switzerland	PROLINE EC 250 prothioconazole (250)	200 g/ha		1	BBCH61
Wheat	Switzerland	PROSARO EC 250 prothioconazole + tebuconazole (125 + 125)	125 g/ha		1	BBCH61
Wheat	Canada United States	PROLINE SC 480 prothioconazole (480)	200 g/ha		1	30
Wheat, winter	Belgium	FANDANGO EC 200 fluoxastrobin + prothioconazole (100 + 100)	150 g/ha	150–300 L/ha	2	BBCH65
Wheat, winter	Belgium	INPUT PRO EC 250 Prothioconazole (250)	200 g/ha		2	35
Wheat, winter	Belgium	FANDANGO EC 200 fluoxastrobin + prothioconazole (100 + 100)	120 g/ha		1	n.a
Wheat, winter	Czech Republic	FANDANGO EC 200 fluoxastrobin + prothioconazole (100 + 100)	150 g/ha	200–400 L/ha	2	35
Wheat, winter	Hungary	PROSARO EC 250 prothioconazole + tebuconazole (125 + 125)	125 g/ha	250–300 L/ha	2	35
Wheat, winter	Ireland	CELLO EC 450 prothioconazole + spiroxamine + tebuconazole (100 + 250 + 100)	125 g/ha	200–300 L/ha	2	BBCH71
Wheat, winter	Ireland	COYOTE EC 300 fluoxastrobin + prothioconazole + trifloxystrobin (75 + 150 + 75)	150 g/ha	200–300 L/ha	2	BBCH71
Wheat, winter	Ireland	FANDANGO EC 200 fluoxastrobin + prothioconazole (100 + 100)	150 g/ha	200–300 L/ha	2	BBCH71
Wheat, winter	Ireland	HELIX EC 460 prothioconazole + spiroxamine (160 + 300)	200 g/ha	200–300 L/ha	3	BBCH71
Wheat, winter	Ireland	METTLE EC 200 fluoxastrobin + prothioconazole (100 + 100)	150 g/ha	200–300 L/ha	2	BBCH71
Wheat, winter	Ireland	PROLINE EC 250 prothioconazole (250)	200 g/ha		3	BBCH71

Crop	Country	Trade name Formulation type/ Content (g/L)	Application			PHI (days)
			Rate	Water	No.	
Wheat, winter	Ireland	PROSARO EC 250 prothioconazole + tebuconazole (125 + 125)	150 g/ha	200–300 L/ha	3	BBCH71
Wheat, winter	Ireland	ZEPHYR SC 263 prothioconazole + trifloxystrobin (175 + 88)	131 g/ha	200–300 L/ha	2	n.a
Wheat, winter	Luxembourg	FANDANGO EC 200 fluoxastrobin + prothioconazole (100 + 100)	150 g/ha	150–300 L/ha	2	BBCH65
Wheat, winter	Luxembourg	INPUT PRO EC 250 prothioconazole (250)	200 g/ha		2	n.a
Wheat, winter	Poland	FANDANGO EC 200 fluoxastrobin + prothioconazole (100 + 100)	100 g/ha	200–400 L/ha	1	n.a
Wheat, winter	Poland	PROSARO EC 250 prothioconazole + tebuconazole (125 + 125)	125 g/ha	200–400 L/ha	1	35
Wheat, winter	Slovakia	FANDANGO EC 200 fluoxastrobin + prothioconazole (100 + 100)	100 g/ha	400 L/ha	1	n.a
Wheat, winter	Slovakia	PROLINE EC 250 prothioconazole (250)	200 g/ha	400 L/ha	1	n.a
Wheat, winter	United Kingdom	CELLO EC 450 prothioconazole + spiroxamine + tebuconazole (100 + 250 + 100)	125 g/ha	200–400 L/ha	2	BBCH71
Wheat, winter	United Kingdom	FANDANGO EC 200 fluoxastrobin + prothioconazole (100 + 100)	150 g/ha	200–400 L/ha	2	BBCH71
Wheat, winter	United Kingdom	HELIX EC 460 prothioconazole + spiroxamine (160 + 300)	200 g/ha	200–300 L/ha	3	BBCH71
Wheat, winter	United Kingdom	JAUNT EC 300 fluoxastrobin + prothioconazole + trifloxystrobin (75 + 150 + 75)	150 g/ha	200–300 L/ha	2	BBCH71
Wheat, winter	United Kingdom	MAESTRO EC 200 fluoxastrobin + prothioconazole (100 + 100)	150 g/ha	200–300 L/ha	2	BBCH71
Wheat, winter	United Kingdom	MOBIUS SC 325 prothioconazole + trifloxystrobin (175 + 150)	175 g/ha		2	BBCH71
Wheat, winter	United Kingdom	PROLINE EC 250 prothioconazole (250)	200 g/ha		3	n.a

Crop	Country	Trade name Formulation type/ Content (g/L)	Application			PHI (days)
			Rate	Water	No.	
Wheat, winter	United Kingdom	PROSARO EC 250 prothioconazole + tebuconazole (125 + 125)	150 g/ha	200–300 L/ha	3	BBCH71
Wheat, winter	United Kingdom	ZEPHYR SC 263 prothioconazole + trifloxystrobin (175 + 88)	175 g/ha		2	BBCH71
Wheat	United States	PROLINE EC 250 prothioconazole (250)	175-200 g/ha		2	30

Table 48 Use pattern of prothioconazole for foliar application in pulses

Crop	Country	Trade name Formulation type/ Content (g/L)	Application			PHI (days)
			Rate	Water rate	No.	
Bean, Tepary Bean, Adzuki Bean, mung Bean, Lima Bean, Rice-Bean	United States	PROLINE SC 480 prothioconazole (480)	200 g/ha		3	7
Chick pea Lentil Pea	Canada United States	PROLINE SC 480 prothioconazole (480)	200 g/ha		3	7
Groundnut (peanut)	United States	PROLINE SC 480 prothioconazole (480)	200 g/ha		4	14[a]
Groundnut (peanut)	United States	PROVOST SC 433 prothioconazole + tebuconazole (143 + 287)	84–112 g/ha		4	14
Soya bean	United States	PROLINE SC 480 prothioconazole (480)	88–105 g/ha	Min. 140 L/ha for ground, 47 L/ha aerial	3	21

[a] Do not feed hay or threshes or allow livestock to graze in treated areas. Applications may be made by ground or aerial spray equipment.

Table 49 Use pattern of prothioconazole for foliar spray application in canola, rape and sugar beet

Crop	Country	Trade name Formulation type/ Content (g/L)	Application			PHI (days)
			Rate	Water rate	No.	
Canola	Canada	PROLINE SC 480 prothioconazole (480)	150–175 g/ha			36
Canola	United States	PROLINE SC 480 prothioconazole (480)	200 g/ha		2	30
Rape	Belgium	PROSARO EC 250 prothioconazole + tebuconazole (125 + 125)	125 g/ha		1	n.a
Rape	Czech Republic	PROLINE EC 250 prothioconazole (250)	175 g/ha	200–400 L/ha	2	56

Crop	Country	Trade name Formulation type/ Content (g/L)	Application			PHI (days)
			Rate	Water rate	No.	
Rape	Czech Republic	PROSARO EC 250 prothioconazole + tebuconazole (125 + 125)	94 g/ha	200–400 L/ha	2	35
Rape	Czech Republic	PROSARO EC 250 prothioconazole + tebuconazole (125 + 125)	125 g/ha	200–400 L/ha	2	35
Rape	Estonia	PROSARO EC 250 prothioconazole + tebuconazole (125 + 125)	125 g/ha	200–400 L/ha	2	56
Rape	France	JOAO EC 250 Prothioconazole (250)	175 g/ha	100–400 L/ha	2	35
Rape	Germany	PROLINE EC 250 prothioconazole (250)	175 g/ha		1	56
Rape	Latvia	PROSARO EC 250 prothioconazole + tebuconazole (125 + 125)	125 g/ha	200–400 L/ha	2	56
Rape	Lithuania	PROSARO EC 250 prothioconazole + tebuconazole (125 + 125)	125 g/ha	200–400 L/ha	2	56
Rape	Luxembourg	PROSARO EC 250 prothioconazole + tebuconazole (125 + 125)	125 g/ha		1	n.a
Rape	Poland	PROLINE EC 250 prothioconazole (250)	175 g/ha	200–400 L/ha	1	BBCH59
Rape	Switzerland	PROLINE EC 250 prothioconazole (250)	175 g/ha		1	BBCH65
Rape	Switzerland	PROSARO EC 250 prothioconazole + tebuconazole (125 + 125)	125 g/ha		1	BBCH65
Rape, winter	Ireland	PROLINE EC 250 prothioconazole (250)	175 g/ha	200–400 L/ha	2	56
Rape, winter	Ireland	PROSARO EC 250 prothioconazole + tebuconazole (125 + 125)	125 g/ha		2	56
Rape, winter	United Kingdom	PROLINE EC 250 prothioconazole (250)	175 g/ha		2	56
Rape, winter	United Kingdom	PROSARO EC 250 prothioconazole + tebuconazole (125 + 125)	125 g/ha	200–300 L/ha	2	56
Rape Indian rape	United States	PROLINE SC 480 prothioconazole (480)	200 g/ha		2	30
Sugar beet	United States	PROLINE SC 480 prothioconazole (480)	150–200 g/ha		3	7

RESIDUES RESULTING FROM SUPERVISED TRIALS ON CROPS

The meeting received information on supervised trials on cereals (barley, wheat and triticale), pulses (bean and pea), oil seed, rape, sugar beet, soybean and peanut. Prothioconazole was applied using an

EC (emulsifiable concentrate) formulation. Additionally, prothioconazole was applied as seed treatment on cereals using a FS (flowable concentrate) formulation.

Methods applied were validated by recovery experiments prior to and concurrent with the residue analyses, by spiking control samples with JAU 6476-desthio in European trials, and with the mixture of prothioconazole and JAU 6576-desthio in North American trials. The total residues of prothioconazole and JAU6476-desthio ('total JAU6476 derived residue') were quantified by HPLC/triple stage quadrupole mass spectrometry. In the method, residues of prothioconazole are converted to JAU 6476-desthio and JAU 6476-sulfonic acid (both expressed as prothioconazole molar equivalents) and summed with unchanged JAU 6476-desthio (expressed as prothioconazole molar equivalents) to give a total prothioconazole derived residue.

In US and Canadian trials two samples were taken from one site. The results are reported, but only the higher residues were selected for estimation of maximum residue levels.

The storage stability was tested with representative matrices. The studies demonstrated the stability of residues under freezer conditions in crops derived from supervised trials evaluated by this Meeting. The maximum storage period prior to the analyses of samples is shown in Tables 50 and 51.

Table 50 Maximum storage period of cereals and rape samples before analysis in Europe

Crop	Maximum storage period (days)
	JAU 6476-desthio
Barley, ear	1016
Barley, grain	975
Barley, green material	1013
Barley, rest of plant	1008
Barley, straw	973
Barley, seed treated	1207
Wheat, ear	638
Wheat, grain	610
Wheat, green material	688
Wheat, rest of plant	638
Wheat, straw	610
Wheat, seed treated	692
Rape, green material	217
Rape, pod	176
Rape, rest of plant	176
Rape, seed	161
Rape, straw	161

Table 51 Maximum storage period of crop samples analysed for total prothioconazole residue from North America before analysis

Crop	Maximum storage period (days)[a]	Period of demonstrated storage stability (days)
Barley, grain	1222	1077
Barley, hay	1214	1078
Barley, straw	1222	1077
Wheat, grain	1197	1077

Crop	Maximum storage period (days)[a]	Period of demonstrated storage stability (days)
Wheat, forage	1169	1049
Wheat, hay	1175	1078
Wheat, straw	1183	1077
Rape, seed	1215	1079
Peanut, nut	1204	1079
Peanut, hay	1202	1078
Bean, seed	538	1077
Pea, seed	511	1077
Sugar beet, roots	376	1078
Sugar beet, tops	383	1078

[a] Time from sample receipt to the last sample extraction.

Pulses (Dried Peas and Dried Beans)

A total of 23 trials on dried peas and dried beans were carried out with three foliar application of SC480 formulation at a target rate of 200 g/ha in Canada (nine) and the USA (14). The interval between applications was nine to 14 days. Dried beans were harvested when the beans were mature (BBCH 89 to 92), which ranged from seven to eight days after the last treatment. As a part of normal agricultural practice for growing beans, the bean plants were cut and allowed to dry in the field for two to eight days prior to collecting the dried beans.

The pre-harvest interval (PHI) for the dried peas and beans is based on the date when the dried peas and beans were cut. The total residues in dried peas and pods were determined.

Table 52 Results of residue trials conducted with prothioconazole on dried peas in North America

Report No Trial No. Doc No Year	Crop *Variety*	Country	Application				Residues		
			FL	No	kg/ha (ai)	kg/hL (ai)	Portion analysed	DALT (days)	Total residue JAU 6476 (mg/kg)
Decline trials									
200956 J6011-02D M-001515-01-1 2002	Pea, field *Sugar Snap*	USA Hood River, Oregon	480 SC	3	0.201–0.205	0.0928–0.105	Seed	0 0 4 4 7 7 14 14 21 21	0.318 0.288 0.426 0.402 0.292 0.328 0.279 0.285 0.310 0.365

Report No Trial No. Doc No Year	Crop *Variety*	Country	Application				Residues		
			FL	No	kg/ha (ai)	kg/hL (ai)	Portion analysed	DALT (days)	Total residue JAU 6476 (mg/kg)
200956 J6019-02D M-001515-01-1 2002	Pea, field *Eiffel*	Canada Edmonton, Alberta	480 SC	3	0.202–0.205	0.191–0.209	Seed	0 0 3 3 7 7 15 15 22 22	0.118 0.102 0.064 0.062 < 0.05 0.053 0.060 < 0.05 < 0.05 0.056
200956 J6023-02D M-001515-01-1 2002	Bean *Pinto*	USA Stilwell, Kansas	480 SC	3	0.203–0.211	0.106–0.108	Seed	0 0 7 7 14 14 21 21	0.163 0.110 0.096 0.053 0.091 0.051 < 0.05 < 0.05
Harvest trials									
200956 J6007-02H M-001515-01-1 2002	Pea, field *Tonic*	USA Ephrata, Washington	480 SC	3	0.202–0.205	0.0998–0.105	Seed	7 7	0.120 0.122
200956 J6008-02H M-001515-01-1 2002	Pea, field *Talbot*	USA Jerome, Idaho	480 SC	3	0.199–0.202	0.105–0.106	Seed	7 7	0.102 0.118
200956 J6009-02H M-001515-01-1 2002	Pea, field *XP8504188*	USA Madras, Oregon	480 SC	3	0.198–0.210	0.0715–0.0719	Seed	7 7	< 0.05 < 0.05
200956 J6010-02H M-001515-01-1 2002	Pea, field *Majorettes*	USA Hermiston, Oregon	480 SC	3	0.196–0.201	0.0766–0.0768	Seed	7 7	< 0.05 < 0.05
200956 J6012-02H M-001515-01-1 2002	Pea, field *Carnival*	USA Campbell, Minnesota	480 SC	3	0.201–0.202	0.108–0.108	Seed	7 7	< 0.05 < 0.05
200956 J6013-02H M-001515-01-1 2002	Pea, field *Trapper*	Canada Branchton Ontario	480 SC	3	0.199–0.206	0.0927–0.0958	Seed	7 7	< 0.05 < 0.05
200956 J6014-02H M-001515-01-1 2002	Pea, field *Eiffel*	Canada Kipp, Alberta	480 SC	3	0.203–0.206	0.201–0.202	Seed	7 7	< 0.05 0.076

Report No Trial No. Doc No Year	Crop *Variety*	Country	Application				Residues		
			FL	No	kg/ha (ai)	kg/hL (ai)	Portion analysed	DALT (days)	Total residue JAU 6476 (mg/kg)
200956 J6015-02H M-001515-01-1 2002	Pea, field *Keoma*	Canada Rosthern, Saskatchewan	480 SC	3	0.197–0.205	0.181–0.203	Seed	7 7	< 0.05 < 0.05
200956 J6016-02H M-001515-01-1 2002	Pea, field *DS Admiral*	Canada Brookdale, Manitoba	480 SC	3	0.195–0.201	0.0848–0.177	Seed	7 7	< 0.05 < 0.05
200956 J6017-02H M-001515-01-1 2002	Pea, field *Delta*	Canada Wakaw, Saskatchewan	480 SC	3	0.199–0.202	0.179–0.183	Seed	7 7	0.655 0.519
200956 J6018-02H M-001515-01-1 2002	Pea, field *Delta*	Canada Rosthern, Saskatchewan	480 SC	3	0.201–0.203	0.182–0.183	Seed	8 8	0.639 0.684
200956 J6020-02H M-001515-01-1 2002	Bean *OAC Thunder*	Canada Lynden, Ontario	480 SC	3	0.196–0.240	0.0667–0.0767	Seed	8 8	< 0.05 < 0.05
200956 J6021-02H M-001515-01-1 2002	Bean *Pinto*	USA Carlyle, Illinois	480 SC	3	0.203–0.206	0.115–0.214	Seed	7 7	< 0.05 < 0.05
200956 J6022-02H M-001515-01-1 2002	Bean *Sanilac*	USA Oxford, Indiana	480 SC	3	0.197–0.210	0.138–0.142	Seed	8 8	< 0.05 < 0.05
200956 J6024-02H M-001515-01-1 2002	Bean *Remington*	USA Eldridge, North Dakota	480 SC	3	0.198–0.204	0.0719–0.0720	Seed	7 7	< 0.05 < 0.05
200956 J6025-02H M-001515-01-1 2002	Bean *Pintos Othello*	Canada Taber, Alberta	480 SC	3	0.194–0.204	0.199–0.200	Seed	7 7	0.137 0.115
200956 J6026-02H M-001515-01-1 2002	Bean *Pinto Beans*	USA Plainview, Texas	480 SC	3	0.196–0.204	0.102–0.139	Seed	7 7	< 0.05 < 0.05
200956 J6027-02H M-001515-01-1 2002	Bean *Othello*	USA Fromberg, Montana	480 SC	3	0.202–0.204	0.0846–0.200	Seed	7 7	0.199 0.288
200956 J6028-02H M-001515-01-1 2002	Bean *Red Kidney*	USA Fresno, California	480 SC	3	0.198–0.205	0.0796–0.0873	Seed	7 7	< 0.05 < 0.05

Report No Trial No. Doc No Year	Crop *Variety*	Country	Application				Residues		
			FL	No	kg/ha (ai)	kg/hL (ai)	Portion analysed	DALT (days)	Total residue JAU 6476 (mg/kg)
200956 J6029-02H M-001515-01-1 2002	Bean *Othello* *Pinto*	USA Ephrata, Washington	480 SC	3	0.202	0.0714–0.0866	Seed	7 7	< 0.05 < 0.05

Sugar beet

Three foliar spray applications of prothioconazole 480 SC were made to sugar beets at a target rate of 200 g/ha/application (actual ranged from 192 to 214 g/ha) using spray volumes ranging from 85 to 187 L/ha. Intervals between applications were from eight to ten days. A non-ionic surfactant (NIS) was added as a spray adjuvant at the lowest labelled rate. All applications were made using ground-based equipment.

Sugar beet tops and roots were harvested when the beets had reached harvestable size (BBCH 49). Sampling was performed at 6–7 and 13–14 days after last treatment. The total residues of prothioconazole and JAU6476-desthio were determined.

Table 53 Results of residue trials conducted with three applications of prothioconazole 480 SC formulations on sugar beet roots in the USA

Report No Trial No. Doc No Year	Crop *Variety*	Country	Application		Residues	
			kg/ha (ai)	kg/hL (ai)	DALT (days)	Total residue prothioconazole (mg/kg)
RAJAY024 JA001-04D M-278843-01-1 2004	Sugar beet *unknown*	USA Springfield, Nebraska	0.201–0.204	0.147–0.149	0 0 7 7 13 13 20 20 27 27	0.070 0.069 0.079 0.238 0.126 < 0.050 < 0.050 0.070 < 0.050 0.062
RAJAY024 JA002-04H M-278843-01-1 2004	Sugar beet *Tonic*	USA Sabin, Minnesota	0.203–0.208	0.197–0.204	6 6 14 14	0.119 0.217 0.137 0.082
RAJAY024 JA003-04H M-278843-01-1 2004	Sugar beet *Talbot*	USA Rockwood, Ontario	0.200–0.214	0.210–0.235	6 6 14 14	< 0.05 < 0.05 < 0.05 < 0.05
RAJAY024 JA004-04H M-278843-01-1 2004	Sugar beet *Hilleshog 2433RZ*	USA Britton, South Dakota	0.199	0.212	7 7 14 14	< 0.05 < 0.05 < 0.05 < 0.05
RAJAY024 JA005-04H M-278843-01-1 2004	Sugar beet *66283* *Medium*	USA Theilman, Minnesota	0.201	0.177	6 6 14 14	< 0.05 < 0.05 < 0.05 < 0.05

Report No Trial No. Doc No Year	Crop *Variety*	Country	Application		Residues	
			kg/ha (ai)	kg/hL (ai)	DALT (days)	Total residue prothioconazole (mg/kg)
RAJAY024 JA006-04H M-278843-01-1 2004	Sugar beet *Crystal 955*	USA Velva, North Dakota	0.196–0.201	0.138–0.143	7 7 14 14	< 0.05 < 0.05 < 0.05 < 0.05
RAJAY024 JA007-04H M-278843-01-1 2004	Sugar beet *Wrangler*	USA Levelland, Texas	0.202–0.208	0.136–0.140	7 7 14 14	< 0.05 < 0.05 < 0.05 < 0.05
RAJAY024 JA008-04H M-278843-01-1 2004	Sugar beet *Beta 8757 LL*	USA Jerome, Idaho	0.199–0.203	0.108–0.110	7 7 14 14	< 0.05 < 0.05 < 0.05 < 0.05
RAJAY024 JA009-04H M-278843-01-1 2004	Sugar beet *Beta 4430R*	USA Porterville, California	0.200–0.202	0.112–0.143	7 7 14 14	0.134 0.067 0.064 0.080
RAJAY024 JA010-04H M-278843-01-1 2004	Sugar beet *Alpine*	USA Fresno, California	0.194–0.208	0.114–0.118	7 7 14 14	< 0.05 < 0.05 0.066 < 0.05
RAJAY024 JA011-04H M-278843-01-1 2004	Sugar beet *Beta 4490R*	USA Rupert, Idaho	0.199–0.202	0.192–0.201	7 7 14 14	< 0.05 < 0.05 < 0.05 < 0.05
RAJAY024 JA012-04H M-278843-01-1 2004	Sugar beet *Beta 4490R*	USA Twin Falls, Idaho	0.198–0.202	0.108–0.115	7 7 14 14	< 0.05 < 0.05 < 0.05 < 0.05

Cereals

A total of 123 trials were carried out on cereals (wheat and barley) with SC 480, EC250 and FS200 formulations in Canada, Europe and the USA.

Wheat

A total of 27 residue trials were conducted on wheat with the FS 200 formulation for seed dressing and the EC 250 formulation for spraying in both European regions. In some trials the FS 200 formulation of the product was used for seed dressing followed by the EC 250 formulation for spray application.

The foliar treatments were performed at BBCH growth stages 32/33 (2–3 nodes developed), 39–41 and 69, respectively, with the last treatment performed 34–36 days prior to the recommended pre-harvest interval (PHI).

Table 54 JAU6476-desthio residues in wheat grain following seed treatment with prothioconazole FS [a] formulation at 1 × 15 g/100 kg seed rate in Europe.

Country Year	Crop *Variety*	DALT [b] [days]	JAU 6476-desthio [mg/kg]	Report No. Trial No. Doc No
Great Britain 1999	Spring Wheat *Chablis*	130	< 0.01	RA-2010/99, R 1999 0173/9 M-073513-01-1
Germany 1999	Spring Wheat *Thasos*	139	< 0.01	RA-2010/99, R 1999 0174/7 M-073513-01-1
Southern France 1999	Spring Wheat *Furio*	155	< 0.01	RA-2010/99, R 1999 0175/5 M-073513-01-1
Southern France 1999	Spring Wheat *Furio*	134	< 0.01	RA-2010/99, R 1999 0176/3 M-073513-01-1
Germany 2000	Spring Wheat *Lavett*	146	< 0.01	RA-2091/00, R 2000 0002/2 M-075017-01-1
Northern France 2000	Spring Wheat *Furio*	149	< 0.01	RA-2091/00, R 2000 0424/9 M-075017-01-1
Southern France 2000	Spring Wheat *Furio*	146	< 0.01	RA-2090/00, R 2000 0003/0 M-073003-01-1
Italy 2000	Spring Wheat *Pandas*	120	< 0.01	RA-2090/00, R 2000 0423/0 M-073003-01-1

[a] FS 200 is a flowable concentrate for seed treatment, containing 200 g/L prothioconazole

[b] Days after last treatment

Table 55 JAU6476-desthio residues in wheat grain deriving from trials conducted with prothioconazole in Northern Europe: seed treatment + spraying

Country Year	Crop *Variety*	FL[a]	Application			DALT [b] [days]	JAU 6476-desthio [mg/kg]	Report No. Trial No. Doc No
			No	kg/ha as	kg/hL as			
Germany 1999	Spring Wheat *Thasos*	200 FS 250EC	1 3	0.027 0.200	 0.067	35 << 51	< 0.01 < 0.01	RA-2003/99 R 1999 0266/2 M-075134-01-1
Germany 1998	Winter Wheat *Bandit*	200 FS 250 EC	1 3	0.027 0.200	 0.067	35 << 50	< 0.01 < 0.01	RA-2003/99 R 1999 0023/6 M-075134-01-1
Germany 1998	Winter Wheat *Bandit*	200 FS 250 EC	1 3	0.027 0.200	 0.067	35 << 46	< 0.01 < 0.01	RA-2003/99 R 1999 0025/2 0025-99
France 1998	Winter Wheat *Sideral*	200 FS 250 EC	1 3	0.027 0.200	 0.067	35 << 43	< 0.01 < 0.01	RA-2003/99 R 1999 0026/ 0026-99
Great Britain 1999	Winter Wheat *Abbot*	250 EC	3	0.200	0.0668	54	< 0.01	RA-2003/99 R 1999 0027/9 0027-99
Germany 2000	Spring Wheat *Vinjett*	250 EC	3	0.200	0.067	64	< 0.01	RA-2104/00 R 2000 0454/0 M-088723-01-1
Germany 2000	Spring Wheat *Lavett*	250 EC	3	0.200	0.067	35 <<	< 0.01	RA-2104/00 R 2000 0457/5 M-088723-01-1
France 2000	Spring Wheat *Furio*	250 EC	3	0.200	0.067	35 << 42	< 0.01 < 0.01	RA-2104/00 R 2000 0474/5 M-088723-01-1

Country Year	Crop *Variety*	FL[a]	Application			DALT [b]	JAU 6476-desthio [mg/kg]	Report No. Trial No. Doc No
			No	kg/ha as	kg/hL as	[days]		
Great Britain 2000	Spring Wheat *Chablis*	250 EC	3	0.200	0.067	35 <<	0.32	RA-2104/00 R 2000 0475/3 M-088723-01-1
Germany 2000	Spring Wheat *Lavett*	250 EC	3	0.200	0.0668	35 <<	< 0.01	RA-2104/00 R 2000 0476/1 M-088723-01-1

[a] 250 EC is an emulsifiable concentrate formulation, containing 250 g/L prothioconazole

[b] Days after last treatment

Table 56 JAU6476-desthio residues in wheat grain deriving from trials conducted with prothioconazole in Southern Europe: seed treatment + spraying

Country Year	Crop *Variety* Variety	FL[a]	Application			DALT[b] [days]	JAU 6476-desthio [mg/kg]	Report No. Trial No Doc No
			No.	kg/ha as	kg/hL as			
France 1998	Winter Wheat *Sideral*	200 FS 250 EC	1 3	0.027 0.169 0.200	 0.0668 0.0668	35 << 40	< 0.01 < 0.01	RA-2149/98 R 1998 1586/1 M-083957-01-1
Spain 1998	Winter Wheat *Adalid*	200 FS 250 EC	1 3	0.023 0.200	 0.0668	28 34 48	< 0.01 < 0.01 < 0.01	RA-2149/98 R 1998 1588/8 M-083957-01-1
Italy 1998	Winter Wheat *MEC*	200 FS 250 EC	1 3	0.024 0.200	 0.0668	28 35 42	< 0.01 < 0.01 < 0.01	RA-2149/98 R 1998 1589/6 M-083957-01-1
France 1998	Winter Wheat *Sideral*	200 FS 250 EC	1 3	0.027 0.200	 0.0668	34 << 50	< 0.01 < 0.01	RA-2149/98 R 1998 1314/1 M-083957-01-1
Spain 1998	Winter Wheat *Soisson*	200 FS 250 EC	1 3	0.022 0.200	 0.0668	28 34 << 48	< 0.01 < 0.01 < 0.01	RA-2149/98 R 1998 1725/2 M-083957-01-1
Spain 2000	Winter Wheat *Sarina*	250 EC	3	0.211 0.200	0.0668 0.0668	35 42	< 0.01 < 0.01	RA-2105/00 R 2000 0455/9 M-088975-01-1
France 2000	Triticale *Magistral*	250 EC	3	0.200	0.0668	35 57	< 0.01 < 0.01	RA-2105/00 R 2000 0478/8 M-088975-01-1
France 2000	Durum Wheat *Orjaune*	250 EC	3	0.200	0.0668	35 49	< 0.01 < 0.01	RA-2105/00 R 2000 479/6 M-088975-01-1
Spain 2000	Winter Wheat *Soissons*	250 EC	3	0.200	0.0668	36 42	< 0.01 < 0.01	RA-2105/00 R 2000 0482/6 M-088975-01-1

[a]: 250 EC is an emulsifiable concentrate formulation, containing 250 g/L prothioconazole

[b]: Days after last treatment

A total of 54 residue trials (52 harvest and two decline) were conducted on wheat with the 480 SC formulation in the USA and Canada. Two foliar spray applications of JAU6476 480 SC were made 14 (±2) days apart to each treated plot at a target rate of 127 g ai/ha (120–143 g ai/ha) for the first application made at BBCH growth stage 34 to 65 (“Node 4 at least 2 cm above node 2” to “full flowering: 50% of anthers mature”) and 202 g ai/ha (190–223 g ai/ha) for the second application

made at BBCH growth stage 59 to 71 (“end of heading; inflorescence fully emerged” to “first grains have reached half their final size”) in target spray volumes ranging from 103 to 421 L/ha. The interval between applications was 13 to 18 days.

The total residues of prothioconazole in forage, hay, grain and straw were determined after two spray applications. From the treated plot of each trial, duplicate composite samples of wheat forage, hay, grain or straw were collected. Both residue values are reported for each of the matrices in Table 57 however only the larger ones were taken into account for estimation of maximum residue levels.

Table 57 Results of decline residue trials conducted with prothioconazole on wheat in the USA and Canada

Report No Trial No. Doc No Year	Crop *Variety*	Country	Application				Residues		
			FL	No	kg/ha (ai)	kg/hL (ai)	Portion analysed	DALT (days)	Total residue prothioconazole (mg/kg)
200524 J6046-00D M-001538-01-1 2000	Wheat *Russ Wheat*	USA New Rockford, North Dakota	480 SC	2			grain	36 36 40 40 46 46 50 50	< 0.02 < 0.02 < 0.02 < 0.02 < 0.02 < 0.02 < 0.02 < 0.02
200524 J6045-00D M-001538-01-1 2001	Wheat *Arapahoe*	USA Louisville Nebraska	480 SC	2	0.127–0.202	0.0778–0.126	grain	35 35 39 39 44 44 49 49	< 0.02 < 0.02 < 0.02 < 0.02 < 0.02 < 0.02 < 0.02 < 0.02

Table 58 Results of residue trials conducted with prothioconazole on wheat in the USA and Canada

Report No Trial No. Doc No Year	Crop *Variety*	Country	Application				Residues		
			FL	No	kg/ha (ai)	kg/hL (ai)	Portion analysed	DALT (days)	total residue prothioconazole (mg/kg)
200524 J6044-00H M-001538-01-1 2000	Wheat *Tahoe*	Canada St. George, Ontario	480 SC	2	0.1350–0.2110	0.061–0.100	grain	42 42	< 0.02 < 0.02
200524 J6047-00H M-001538-01-1 2000	Wheat *Penawawa*	USA Hermiston, Oregon	480 SC	2	0.129–0.206	0.044–0.070	grain	42 42	< 0.02 < 0.02
200524 J6048-00H M-001538-01-1 2001	Wheat *Ogallala*	USA Uvalde, Texas	480 SC	2	0.130–0.196	0.069–0.116	grain	42 42	< 0.02 < 0.02

Report No Trial No. Doc No Year	Crop *Variety*	Country	Application				Residues		
			FL	No	kg/ha (ai)	kg/hL (ai)	Portion analysed	DALT (days)	total residue prothioconazole (mg/kg)
200524 J6049-00H M-001538-01-1 2001	Wheat *Jagger*	USA Claude, Texas	480 SC	2	0.128–0.207	0.064–0.103	grain	41 41	< 0.02 < 0.02
200524 J6050-00H M-001538-01-1 2001	Wheat *Custer*	USA Cordell, Oklahoma	480 SC	2	0.123–0.203	0.099–0.158	grain	38 38	< 0.02 < 0.02
200524 J6051-00H M-001538-01-1 2001	Wheat *Custer*	USA Frederick, Oklahoma	480 SC	2	0.120–0.198	0.064–0.102	grain	10 10	< 0.02 < 0.02
200524 J6052-00H M-001538-01-1 2001	Wheat *Tam 200*	USA Hart, Texas	480 SC	2	0.127–0.201	0.084–0.135	grain	35 35	< 0.02 < 0.02
200524 J6053-00H M-001538-01-1 2000	Wheat *2375*	USA Velva, North Dakota	480 SC	2	0.128–0.201	0.045–0.0720	grain	33 33	< 0.02 < 0.02
200524 J6054-00H M-001538-01-1 2001	Wheat *Tam 202, Lot Star 10*	USA Levelland, Texas	480 SC	2	0.127–0.202	0.067–0.107	grain	43 43	< 0.02 < 0.02
200524 J6055-00H M-001538-01-1 2000	Wheat *Alsen*	USA Ellendale, North Dakota	480 SC	2	0.126–0.202	0.068–0.108	grain	39 39	< 0.02 < 0.02
200524 J6056-00H M-001538-01-1 2000	Wheat *Forge spring wheat*	USA Lake Andes, South Dakota	480 SC	2	0.126–0.201	0.071–0.112	grain	46 46	< 0.02 0.026
200524 J6057-00H M-001538-01-1 2000	Wheat *Tahoe*	Canada Paris, Ontario	480 SC	2	0.1440–0.2000	0.061–0.100	grain	42 42	< 0.02 < 0.02
200524 J6058-00H M-001538-01-1 2001	Wheat *Mit*	USA East Bernard, Texas	480 SC	2	0.126–0.196	0.090–0.138	grain	32 32	< 0.02 < 0.02
200524 J6059-00H M-001538-01-1 2001	Wheat *Karl 92*	USA Stilwell, Kansas	480 SC	2	0.129–0.202	0.06–0.106	grain	42 42	< 0.02 < 0.02
200524 J6060-00H M-001538-01-1 2001	Wheat *Becks 107*	USA Oxford, Indiana	480 SC	2	0.130–0.203	0.093–0.147	grain	43 43	< 0.02 < 0.02

Report No Trial No. Doc No Year	Crop *Variety*	Country	Application				Residues		
			FL	No	kg/ha (ai)	kg/hL (ai)	Portion analysed	DALT (days)	total residue prothioconazole (mg/kg)
200524 J6061-00H M-001538-01-1 2000	Wheat *Barrie*	Canada Red Deer, Alberta	480 SC	2	0.1260–0.2110	0.043–0.070	grain	57 57	< 0.02 < 0.02
200524 J6062-00H M-001538-01-1 2000	Wheat *HRS wheat prodigy*	Canada Monarch, Alberta	480 SC	2	0.1270–0.2020	0.032–0.051	grain	30 30	0.051 0.040
00524 J6063-00H M-001538-01-1 2001	Wheat *Pioneer 2684*	USA Benoit, Mississippi	480 SC	2	0.123–0.205	0.079–0.120			
							Grain	42 42	< 0.02 < 0.02
200524 J6064-00H M-001538-01-1 2001	Wheat *Cooker 107*	USA Knightdale, North Carolina	480 SC	2	0.126–0.199	0.040–0.062	grain	37 37	< 0.02 < 0.02
200524 J6066-00H M-001538-01-1 2000	Wheat *AC Cora*	Canada Minto, Manitoba	480 SC	2	0.1330–0.2100	0.032–0.051	grain	47 47	< 0.02 < 0.02
200524 J6067-00H M-001538-01-1 2000	Wheat *AC Cora*	Canada Minto, Manitoba	480 SC	2	0.1319–0.2070	0.032–0.050	grain	49 49	< 0.02 < 0.02
200524 J6068-00H M-001538-01-1 2000	Wheat *AC Barrie*	Canada Wakaw, Saskatchewan	480 SC	2	0.1290–0.1970	0.118–0.18	grain	55 55	< 0.02 < 0.02
200524 J6069-00H M-001538-01-1 2000	Wheat *McKenzie*	Canada Leask, Saskatchewan	480 SC	2	0.1250–0.2010	0.032–0.05	grain	48 48	< 0.02 < 0.02
200524 J6070-00H M-001538-01-1 2000	Wheat *AC Cadillac*	Canada Rostern, Saskatchewan	480 SC	2	0.1260–0.1950	0.032–0.050	grain	53 53	< 0.02 < 0.02
200524 J6071-00H M-001538-01-1 2000	Wheat *Barrie (certified)*	Canada Brookdale, Manitoba	480 SC	2	0.1280–0.2040	0.114–0.184	grain	43 43	0.025 0.040
200524 J6072-00H M-001538-01-1 2000	Wheat *Barrie*	Canada Lacombe, Alberta	480 SC	2	0.1260–0.2010	0.042–0.067	grain	57 57	< 0.02 < 0.02
200524 J6073-00H M-001538-01-1 2000	Wheat *AC Barrie*	Canada Delisle, Saskatchewan	480 SC	2	0.1270–0.2000	0.032–0.050	grain	38 38	< 0.02 < 0.02

Report No Trial No. Doc No Year	Crop *Variety*	Country	Application				Residues		
			FL	No	kg/ha (ai)	kg/hL (ai)	Portion analysed	DALT (days)	total residue prothioconazole (mg/kg)
200524 J6074-00H M-001538-01-1 2000	Wheat *Prodigy*	Canada Delisle, Saskatchewan	480 SC	2	0.1260–0.2000	0.032–0.051	grain	43 43	< 0.02 < 0.02
200524 J6075-00H M-001538-01-1 2000	Wheat *HRS wheat prodigy*	Canada Warner, Alberta	480 SC	2	0.1240–0.2050	0.031–0.050	grain	31 31	0.029 0.040
200524 J6076-00H M-001538-01-1 2000	Wheat *Prodigy*	Canada Coaldale, Alberta	480 SC	2	0.1250–0.1980	0.032–0.050	grain	35 35	< 0.02 0.024
200524 J6077-00H M-001538-01-1 2000	Wheat *Prodigy*	Canada Kipp, Alberta	480 SC	2	0.1260–0.2000	0.032–0.051	grain	30 30	0.028 0.061

Barley

A total of 17 residue trials were conducted on barley with the FS 200 formulation for seed dressing and the EC 250 formulation for spraying in both European regions.

The actual dressing rate was 12 to 14 g of prothioconazole per 100 kg seed, corresponding to 20.2 to 23.6 g JAU 6476/ha. The foliar treatments were conducted at growth stages 37–49 and 59–71.

Table 59 Residues in barley grain derived from residue trials conducted with prothioconazole on barley in Northern Europe

Country Year	Crop *Variety*	FL [a]	Application			DALT [c] [days]	JAU 6476-desthio [mg/kg]	Report No. Trial No. Doc No
			No	kg/ha as	kg/hL as			
Germany 1998	Spring Barley *Scarlett*	200 FS 250 EC	1 2	150 [b] 0.200 0.400	0.0668 0.1333	57	< 0.01	RA-2150/98 R 1998 1256/0 M-073128-02-1
Germany 1998	Spring Barley *Scarlett*	200 FS 250 EC	1 2	150 0.200	0.0668	59	< 0.01	RA-2140/98 R 1998 1580/2 M-073128-02-1
Germany 1998	Spring Barley *Scarlett*	200 FS 250 EC	2	150 0.200	0.0668	57	< 0.01	RA-2140/98 R 1998 1247/1 M-073128-02-1
France 1998	Spring Barley *Prisma*	200 FS 250 EC	2	150 0.200	0.0715	48	< 0.01	RA-2140/98 R 1998 1581/0 M-072786-02-1
Great Britain 1998	Spring Barley *Alexis*	200 FS 250 EC	2	150 0.200	0.0668	51	< 0.01	RA-2140/98 R 1998 1582/9 M-072786-02-1
Sweden 2000	Spring Barley *Henni*	250 EC	2	0.200	0.0668	35<<	< 0.01	RA-2101/00 R 2000 0452/4 M-072786-02-1
France 2000	Spring Barley *Nevada*	250 EC	2	0.200	0.0668	56	< 0.01	RA-2101/00 R 2000 0462/1 M-086237-01-1

Country Year	Crop *Variety*	FL [a]	Application			DALT [c] [days]	JAU 6476-desthio [mg/kg]	Report No. Trial No. Doc No
			No	kg/ha as	kg/hL as			
Great Britain 2000	Spring Barley *Optic*	250 EC	2	0.200	0.0668	57	< 0.01	RA-2101/00 R 2000 0464/8 M-086237-01-1
Germany 2000	Spring Barley *Alexis*	250 EC	2	0.200	0.0668	55	< 0.01	RA-2101/00 R 2000 0465/6 M-086237-01-1

[a] 200 FS is a flowable concentrate for seed treatment, containing 200 g/L prothioconazole; 250 EC is an emulsifiable concentrate formulation, containing 250 g/L prothioconazole

[b.] The nominal application rate of seed treatment is given for FS formulations in mg ai/kg, but the dimension is not indicated.

[c] Days after last treatment<< relevant PHI

Table 60 Residues in barley grain derived from residue trials conducted with prothioconazole on barley in Southern Europe

Country Year	Crop *Variety*	FL[a]	Application			DALT[b] [days]	JAU 6476-desthio [mg/kg]	Report No. Trial No. Doc No.
			No.	kg/ha as	kg/hL as			
France 1998	Spring Barley *Volga*	200 FS 250 EC	 2	150 0.200	0.0668	35 << 48	0.02 0.02	RA-2079/98 R 1998 1249/8 M-075011-01-1
France 1998	Winter Barley *Vertige*	250 EC	2	0.200	0.0668	48	0.01	RA-2144/98 R 1998 1317/6 M-072984-02-1
France 1998	Winter Barley *Pilastro*	250 EC	2	0.200	0.0668	35 << 41	< 0.01 < 0.01	RA-2144/98 R 1998 1571/3 M-072984-02-1
France 1998	Winter Barley *Carina*	250 EC	2	0.200	0.0668	57	0.02	RA-2144/98 R 1998 1572/1 M-072984-02-1
Spain 2000	Spring Barley *Graphic*	250 EC	2	0.217 0.200	0.0668 0.0668	35 << 41	< 0.01 < 0.01	RA-2103/00 R 2000 0453/2 M-086807-01-1
Italy 2000	Spring Barley *Patty*	250 EC	2	0.200	0.0668	35 << 49	0.01 0.02	RA-2103/00 R 2000 0470/2 M-086807-01-1
France 2000	Spring Barley *Nevada*	250 EC	2	0.200	0.0668	35 << 42	0.01 0.01	RA-2103/00 R 2000 0472/9 M-086807-01-1
France 2000	Spring Barley *Nevada*	250 EC	2	0.200	0.0668	35 << 52	0.02 0.01	RA-2103/00 R 2000 0473/7 M-086807-01-1

[a] 200 FS is a flowable concentrate for seed treatment, containing 200 g/L prothioconazole, 250 EC is an emulsifiable concentrate formulation, containing 250 g/L prothioconazole

[b] Days after last treatment;<< relevant PHI

A total of 25 residue trials (23 harvest and 2 decline) were conducted with two foliar applications with 480 SC formulation on barley in the USA and Canada. The first application rate was made at the growth stage BBCH 45 to 47 at a target rate of 123 g ai/ha (120–143 g ai/ha) using spray volumes ranging from 187 to 468 L/ha.

The second application was made at full flowering BBCH 65 (± 2 days) at a target rate of 202 g ai/ha (190–213 g ai/ha) using spray volumes ranging from 187 to 468 L/ha. The interval between applications was 5 to 27 days.

Table 61 Results of residue trials conducted with prothioconazole on barley in the USA and Canada

Report No Trial No. Doc No Year	Crop *Variety*	Country	Application				Residues		
			FL	No	kg/ha (ai)	kg/hL (ai)	Portion analysed	DALT (days)	Total residue prothioconazole (mg/kg)
200806 J6001-00D M-000715-01-1 2000	Barley *Robust*	USA Northwood North Dakota	480 SC	2	0.1280–0.2020	0.0621–0.0973	grain	32 32 37 37 44 44 47 47	0.036 0.044 0.041 0.047 0.044 0.049 < 0.02 0.028
200806 J6008-00D M-000715-01-1 2000	Barley *Chapais*	Canada Branchton, Ontario	480 SC	2	0.1280–0.2020	0.0621–0.0973	grain	36 36 39 39 45 45 49 49	0.033 0.020 0.045 0.036 0.028 0.028 0.037 0.022
200806 J6002-00H M-000715-01-1 2000	Barley *Steptoe*	USA Hermiston Oregon	480 SC	2	0.124–0.206	0.0460–0.0700	grain	42 42	< 0.02 < 0.02
200806 J6003-00H M-000715-01-1 2001	Barley *Baretta*	USA Maricopa, Arizona	480 SC	2	0.131–0.206	0.0461–0.0732	grain	48 48	0.088 0.082
200806 J6004-00H M-000715-01-1 2001	Barley *Baretta*	USA Wilcox, Arizona	480 SC	2	0.126–0.195	0.0452–0.0724	grain	71 71	0.059 0.083
200806 J6005-00H M-000715-01-1 2000	Barley *Robust*	USA Velva, North Dakota	480 SC	2	0.128–0.203	0.0455–0.0723	grain	33 33	< 0.02 < 0.02
200806 J6006-00H M-000715-01-1 2000	Barley *Robust*	USA New Rockford, North Dakota	480 SC	2	0.126–0.212	0.0444–0.0750	grain	36 36	0.031 0.035
200806 J6007-00H M-000715-01-1 2000	Barley *Robust*	USA Ellendale, North Dakota	480 SC	2	0.128–0.202	0.0676–0.107	grain	43 43	< 0.02 < 0.02
200806 J6009-00H M-000715-01-1 2000	Barley *Morex*	USA Jerome, Idaho	480 SC	2	0.126–0.204	0.0452–0.0727	grain	43 43	< 0.02 < 0.02

Report No Trial No. Doc No Year	Crop *Variety*	Country	Application				Residues		
			FL	No	kg/ha (ai)	kg/hL (ai)	Portion analysed	DALT (days)	Total residue prothioconazole (mg/kg)
200806 J6010-00H M-000715-01-1 2000	Barley *Robust*	USA Northwood, North Dakota	480 SC	2	0.126–0.201	0.0450–0.0715	grain	44 44	0.027 0.031
200806 J6013-00H M-000715-01-1 2000	Barley *AC Stephen*	USA Germans-ville, Pennsylvania	480 SC	2	0.131–0.197	0.0384–0.0653	grain	57 57	0.022 < 0.02
200806 J6078-00H M-000715-01-1 2000	Barley *Robust*	Canada Minto, Manitoba	480 SC	2	0.1260–0.2060	0.03190–0.05066	grain	36 36	0.138 0.132
200806 J6079-00H M-000715-01-1 2000	Barley *Robust*	Canada Minto, Manitoba	480 SC	2	0.1280–0.1940	0.03206–0.05075	grain	32 32	0.144 0.158
200806 J6080-00H M-000715-01-1 2000	Barley *AC Rosser*	Canada Brookdale, Manitoba	480 SC	2	0.1310–0.2020	0.1152–0.1833	grain	43 43	0.052 0.061
200806 J6081-00H M-000715-01-1 2000	Barley *Bedford*	Canada Clanwilliam Manitoba	480 SC	2	0.1270–0.2040	0.1158–0.1826	grain	65 65	0.022 0.030
200806 J6082-00H M-000715-01-1 2000	Barley *AC Metcalf*	Canada Marcelin, Saskatchewan	480 SC	2	0.1240–0.2010	0.03156–0.05085	grain	48 48	< 0.02 < 0.02
200806 J6083-00H M-000715-01-1 2000	Barley *Harrington*	Canada Rosthem, Saskatchewan	480 SC	2	0.1270–0.2010	0.03154–0.05012	grain	43 43	< 0.02 < 0.02
200806 J6084-00H M-000715-01-1 2000	Barley *Harrington*	Canada Wakaw, Saskatchewan	480 SC	2	0.1270–0.2000	0.1162–0.1838	grain	34 34	< 0.02 < 0.02
200806 J6085-00H M-000715-01-1 2001	Barley *Wheat*	Canada Lacombe, Alberta	480 SC	2	0.1390–0.2110	0.1383–0.2110	grain	71 71	< 0.02 n.a.
200806 J6086-00H M-000715-01-1 2001	Barley *Wheat*	Canada Penhold, Alberta	480 SC	2	0.1330–0.2120	0.1325–0.2109	grain	71 71	< 0.02 < 0.02
200806 J6087-00H M-000715-01-1 2000	Barley *Stein*	Canada Rosthem, Saskatchewan	480 SC	2	0.1240–0.2052	0.1150–0.1832	grain	52 52	< 0.02 < 0.02

Report No Trial No. Doc No Year	Crop *Variety*	Country	Application				Residues		
			FL	No	kg/ha (ai)	kg/hL (ai)	Portion analysed	DALT (days)	Total residue prothioconazole (mg/kg)
200806 J6088-00H M-000715-01-1 2000	Barley *AC Harper*	Canada Kipp, Alberta	480 SC	2	0.1270–0.2090	0.06331	grain	47 47	< 0.02 < 0.02
200806 J6089-00H M-000715-01-1 2000	Barley *Lacombe*	Canada Leduc, Alberta	480 SC	2	0.1290–0.2090	0.1130–0.1833	grain	33 33	< 0.02 0.022
200806 J6090-00H M-000715-01-1 2000	Barley *Excel*	Canada Delisle, Saskatchewan	480 SC	2	0.1270–0.2010	0.03201–0.05109	grain	30 30	0.050 0.094
200806 J6091-00H M-000715-01-1 2000	Barley *Chapais*	Canada St-Paul-d'Abbotsford, Quebec	480 SC	2	0.1390–0.2090	0.281–0.465	grain	36 36	0.102 0.109

Rape seed

A total of 34 trials on rape/canola were carried out with EC250 or SC 480 formulations. The trials were performed in Canada (16), France (7), Germany (2), Great Britain (2), Sweden (1) and the USA (6). The rape was sprayed twice at a product rate of 0.163 to 0.175 kg ai/ha (spray concentration: 0.233%). The applications were performed at BBCH growth stages 51–57 and 67–78, respectively, with the last treatment performed 55 to 59 days prior to harvest (PHI).

Table 62 JAU-desthio residues in rape seed following two applications with 250 EC

Country Year	Crop Variety	Application			DALT [a] [days]	JAU 6476-desthio [mg/kg]	Report No. Trial No. Doc No
		No.	kg/ha ai	kg/hL ai			
Germany 2000	Rape seed	2	0.175	0.0583	67	< 0.01	RA-2088/00 R 2000 0079/0 M-091148-01-1
Sweden 2000	Rape seed	2	0.175	0.0583	67	< 0.01	RA-2088/00 R 2000 0419/2 M-091148-01-1
Great Britain 2000	Rape seed	2	0.190 0.175	0.0583	56 63	0.01 0.01	RA-2088/00 R 2000 0421/4 M-091148-01-1
Germany 2001	Rape seed *Express*	2	0.175	0.0583	57 61	< 0.01 < 0.01	RA-2178/01 R 2001 0515/0 M-035525-01-1
Great Britain 2001	Rape seed *Madrigal*	2	0.175 0.163	0.0583	56	< 0.01	RA-2178/01 R 2001 0516/9 M-035525-01-1
France 2001	Rape seed *Zenith*	2	0.175	0.0583	059	< 0.01	RA-2178/00 R 2001 0517/7 M-035525-01-1
France 2001	Rape seed *Capitole*	2	0.190 0.175	0.0583	56	0.02	RA-2178/00 R 2001 0518/5 M-035525-01-1

Country Year	Crop Variety	Application			DALT [a] [days]	JAU 6476-desthio [mg/kg]	Report No. Trial No. Doc No
		No.	kg/ha ai	kg/hL ai			
France 2000	Rape seed *Olara*	2	0.175	0.0583	56 65	< 0.01 < 0.01	RA-2089/00 R 2000 0080/4 M-074984-01-1
France 2000	Rape seed *Ebonite*	2	0.175	0.0583	55	< 0.01	RA-2089/00 R 2000 0422/2 M-074984-01-1
France 2001	Rape seed *Capitole*	2	0.175	0.0583	56	0.01	RA-2179/01 R 2001 0519/3 M-033374-01-1
France 2001	Rape seed *Constan*	2	0.175	0.0583	56	0.01	RA-2179/01 R 2001 0520/7 M-033374-01-1

[a] Days after last treatment;

In the North American trials two foliar spray applications of prothioconazole 480 SC were made to canola at a target rate of 202 g/ha/application (actual ranged from 190 to 213 g/ha) using spray volumes ranging from 150 to 384 L/ha. All applications were made using ground-based equipment. The first application was made at BBCH 51 to 53 (flower buds visible to flower buds raised above the youngest leaves), and the second application was made at BBCH 65 ± 2 days (full flowering). The interval between applications was 7 to 44 days. Canola seed was harvested from the treated plots at earliest commercial harvest (BBCH growth stage 83) which ranged from 36 to 83 days after the last treatment.

Table 63 Results of residue trials conducted on prothioconazole on rape seed in Canada and the USA

Report No Trial No. Doc No Year	Crop *Variety*	Country	Application				Residues		
			FL	No	kg/ha (ai)	kg/hL (ai)	Portion analysed	DALT (days)	Total residue prothioconazole (mg/kg)
200464 J6128-00D M-0599785-01-1 2000	Rape *Phoenix*	USA Jerome, Idaho	480 SC	2	0.201– 0.202	0.0717– 0.0762	Seed	50 50 54 54 59 59 64 64	< 0.02 < 0.02 < 0.02 < 0.02 < 0.02 < 0.02 < 0.02 < 0.02
200464 J6131-00D M-0599785-01-1 2000	Rape *Invigor 2473L*	Canada Branchton, Ontario	480 SC	2	0.2020– 0.2080	0.1005– 0.1018	Seed	41* 41 41 41 41 41 41 41	< 0.02 < 0.02 < 0.02 < 0.02 < 0.02 < 0.02 < 0.02 < 0.02
200464 J6014-00H M-0599785-01-1 2000	Rape *Quest*	Canada Bethany, Manitoba	480 SC	2	0.1980– 0.2090	0.1830– 0.1841	Seed	56 56	< 0.02 < 0.02
200464 J6015-00H M-0599785-01-1 2000	Rape *Exceed*	Canada Dundern, Saskatchewan	480 SC	2	0.1990– 0.2020	0.1824– 0.1826	Seed	54 54	< 0.02 < 0.02

Report No Trial No. Doc No Year	Crop *Variety*	Country	Application				Residues		
			FL	No	kg/ha (ai)	kg/hL (ai)	Portion analysed	DALT (days)	Total residue prothioconazole (mg/kg)
200464 J6016-00H M-0599785-01-1 2000	Rape *45A51*	Canada Brookdale, Manitoba	480 SC	2	0.2020	0.1828–0.1831	Seed	55 55	< 0.02 < 0.02
200464 J6017-00H M-0599785-01-1 2000	Rape *45A71*	Canada Wakaw, Saskatchewan	480 SC	2	0.2000–0.2040	0.1830–0.1846	Seed	59 59	< 0.02 < 0.02
200464 J6018-00H M-0599785-01-1 2000	Rape *SW Legion*	Canada Hepburn, Saskatchewan	480 SC	2	0.1930–0.2010	0.0507–0.0509	seed	61 61	< 0.02 < 0.02
200464 J6019-00H M-0599785-01-1 2000	Rape *46A76*	Canada Rosthern, Saskatchewan	480 SC	2	0.1990–0.2020	0.1825–0.1843	seed	63 63	< 0.02 < 0.02
200464 J6020-00H M-0599785-01-1 2000	Rape *Quest*	Canada Blaine Lake, Saskatchewan	480 SC	2	0.2020–0.2050	0.1839–0.1840	seed	69 69	< 0.02 < 0.02
200464 J6021-00H M-0599785-01-1 2000	Rape *LG3235*	Canada Lacombe, Alberta	480 SC	2	0.1960–0.2040	0.1009–0.1010	seed	48 48	< 0.02 < 0.02
200464 J6022-00H M-0599785-01-1 2000	Rape *Round up ready, Quest*	Canada Kemnay, Manitoba	480 SC	2	0.2060–0.2110	0.1828–0.1836	seed	56 56	< 0.02 < 0.02
200464 J6023-00HA M-0599785-01-1 2000	Rape *2273 invigor*	Canada Carberry, Manitoba	480 SC	2	0.1930–0.2030	0.1822–0.1832	seed	71 71	0.029 < 0.02
200464 J6024-00H M-0599785-01-1 2000	Rape *Q2*	Canada Kipp, Alberta	480 SC	2	0.1970	0.1003–0.1004	seed	36 36	0.022 0.045
200464 J6025-00H M-0599785-01-1 2000	Rape *Agassiz*	Canada Leduc, Alberta	480 SC	2	0.2010–0.2030	0.1835–0.1839	seed	83 83	< 0.02 < 0.02
200464 J6026-00H M-0599785-01-1 2000	Rape *Agassiz*	Canada Gwyne, Alberta	480 SC	2	0.1970–0.1990	0.1819–0.1841	seed	73 73	< 0.02 < 0.02
200464 J6027-00H M-0599785-01-1 2000	Rape *46A65*	Canada Glenboro, Manitoba	480 SC	2	0.1960–0.2000	0.1832–0.1842	seed	57 57	< 0.02 < 0.02

Report No Trial No. Doc No Year	Crop *Variety*	Country	Application				Residues		
			FL	No	kg/ha (ai)	kg/hL (ai)	Portion analysed	DALT (days)	Total residue prothioconazole (mg/kg)
200464 J6125-00H M-0599785-01-1 2001	Rape *Flint*	USA Chula, Georgia	480 SC	2	0.201–0.202	0.0746–0.0809	seed	78 78	< 0.02 < 0.02
200464 J6126-00H M-0599785-01-1 2000	Rape *Quantum*	USA Northwood, North Dakota	480 SC	2	0.203–0.214	0.0717–0.0728	seed	43 43	< 0.02 < 0.02
200464 J6127-00H M-0599785-01-1 2000	Rape *Quantum*	USA New Rockford, North Dakota	480 SC	2	0.204–0.210	0.0734–0.0752	seed	36 36	< 0.02 < 0.02
200464 J6129-00H M-0599785-01-1 2000	Rape *Raide RR*	USA Ashton, Idaho	480 SC	2	0.198–0.202	0.123–0.130	seed	55 55	< 0.02 < 0.02
200464 J6130-00HA M-0599785-01-1 2001	Rape *Chinook*	USA Ashton, Idaho	480 SC	2	0.194–0.205	0.114–0.117	seed	37 37	0.074 0.097
200464 J6132-00H M-0599785-01-1 2000	Rape *46A74*	Canada Melfort, Saskatchewan	480 SC	2	0.2000–0.2030	0.1813-–0.1829	seed	58 58	< 0.02 < 0.02

Peanuts

A total of 12 trials on peanuts were carried out with SC 480 in the USA. Four foliar spray applications of prothioconazole 480 SC were made to peanuts at a target rate of 202 g/ha/application (actual rate ranged from 202 to 213 g/ha) using spray volumes ranging from 122 to 346 L/ha. The interval between applications was 12 to 15 days. All applications were made using ground-based equipment. Samples were collected at 14 ± 1 days PHI.

As a part of normal agricultural practice for growing peanuts, following digging, the peanuts with shells and the peanut hay samples were both allowed to dry in the field for five to eight days prior to collecting the samples (except for trial J6040-00H in which the samples were only dried for two days due to the threat of rain). The PHI for the peanuts and peanut hay is based on the date that the peanut plants were dug. The total residues of JAU prothioconazole in peanut nutmeat and hay were determined.

Table 64 Total residues in peanut meat deriving from residue trials conducted with four applications 480 SC formulation of prothioconazole in the USA

Report No Trial No. Doc No Year	Crop *Variety*	Country	Application		Residues	
			kg/ha (ai)	kg/hL (ai)	DALT (days)	Total residue prothioconazole (mg/kg)
200508 J6029-00D M-001548-01-1 2000	Peanut *Georgia Greens*	USA Tifton, Georgia	0.202	0.137–0.148	7 7 14 14 21 21 28 28	< 0.02 < 0.02 < 0.02 < 0.02 < 0.02 < 0.02 < 0.02 < 0.02
200508, J6030-00H M-001548-01-1 2000	Peanut *VA 98R*	USA Suffolk, Virginia	0.203–0.208	0.0962–0.107	14 14	< 0.02 < 0.02
200508, J6031-00H M-001548-01-1 2000	Peanut *NC 12C, Lot G-2204*	USA Jamesville North Carolina	0.202–0.203	0.0702–0.0776	13 13	< 0.02 < 0.02
200508, J6032-00H M-001548-01-1 2000	Peanut *VA-C-92R, CV92R54399*	USA Roper, North Carolina	0.197–0.199	0.0707–0.0778	13 13	< 0.02 < 0.02
200508, J6033-00H M-001548-01-1 2000	Peanut *Georgia Green*	USA Inaha, Georgia	0.197–0.203	0.148–0.161	15 15	< 0.02 < 0.02
200508, J6034-00H M-001548-01-1 2000	Peanut *AgraTech 201*	USA Herod, Georgia	0.201–0.204	0.158–0.165	14 14	< 0.02 < 0.02
200508, J6035-00H M-001548-01-1 2000	Peanut *Georgia Green*	USA Columbia, Alabama	0.201–0.203	0.154–0.171	15 15	< 0.02 < 0.02
200508, J6036-00H M-001548-01-1 2000	Peanut *VA 98R*	USA Knightdale, North Carolina	0.201–0.207	0.0601–0.0670	15 15	< 0.02 < 0.02
200508, J6037-00H M-001548-01-1 2000	Peanut *Georgia Green*	USA Vero Beach, Florida	0.202–0.204	0.133–0.141	14 14	< 0.02 < 0.02
200508, J6038-00H M-001548-01-1 2000	Peanut *TAMRun*	USA Vernon, Texas	0.201–0.206	0.0576–0.0645	14 14	< 0.02 < 0.02
200508, J6039-00H M-001548-01-1 2000	Peanut *TAMRun*	USA Vernon, Texas	0.201–0.203	0.0575–0.0643	14 14	< 0.02 < 0.02
200508, J6040-00H M-001548-01-1 2000	Peanut *Spanco*	USA Eakly, Oklahoma	0.202–0.211	0.154–0.161	15 15	< 0.02 < 0.02

Soya bean

Three foliar spray applications of JAU6476 480 SC were made to soya beans at a target rate of 150 g/ha/application (actual ranged from 145 to 188 g/ha) using spray volumes ranging from 85 to

187 L/ha. Intervals between applications were from 7 to 11 days. All applications were made using ground-based equipment. A non-ionic surfactant was added as a spray adjuvant at the lowest labelled rate.

Duplicate treated samples of soya bean forage and hay were collected at PHIs ranging from 5 to 7 days and seed was collected at PHIs ranging from 19 to 23 days. The total residues of JAU6476 and JAU6476-desthio were determined.

Table 65 Residues in soya bean seed derived from residue trials conducted with three applications of prothioconazole 480 SC in the USA

Report No Trial No. Doc No Year	Crop *Variety*	Country	Application			Residues		
			kg/ha (ai)	kg/hL (ai)	GS	Portion analysed	DALT (days)	Total residue prothioconazole (mg/kg)
RAJAY026 JA014-04D-P2 M-270206-01-1 2004	Soya *Pioneer 96M20*	USA Molino, Florida	0.145–0.151	0.100–0.103	88	seed	7 7 14 14 21 21 28 28 35 35	< 0.05 < 0.05 < 0.05 < 0.05 < 0.05 < 0.05 < 0.05 < 0.05 < 0.05 < 0.05
RAJAY026 JA019-04D-P2 M-270206-01-1 2004	Soya *Stine 2788*	USA Seymour, Illinois	0.151–0.154	0.115–0.117	89	seed	7 7 13 13 19 19 27 27 34 34	< 0.05 < 0.05 < 0.05 < 0.05 < 0.05 < 0.05 < 0.05 < 0.05 < 0.05 < 0.05
RAJAY026 JA015-04H-P2 M-270206-01-1 2004	Soya *Pioneer RR 97B52*	USA Tifton, Georgia	0.1421–0.1499	0.1006–0.1053	80	seed	21 21	< 0.05 < 0.05
RAJAY026 JA016-04H-P2 M-270206-01-1 2004	Soya *Pioneer 9492RR*	USA Leland, Mississippi	0.1496–0.1569	0.0972–0.1020	79	seed	20 20	< 0.05 0.055
RAJAY026 JA017-04H-P2 M-270206-01-1 2004	Soya *DP 5915 RR*	USA Washington, Louisiana	0.1497–0.1573	0.0767–0.0957	81	seed	21 21	< 0.05 < 0.05
RAJAY026 JA018-04H M-270206-01-1 2004	Soya *DP5634RR*	USA Proctor, Arkansas	0.1493–0.1503	0.1069–0.1082	79	seed	21 21	0.060 < 0.05
RAJAY026 JA020-04H M-270206-01-1 2004	Soya *Fontanelle 431RR*	USA Stilwell, Kansas	0.1493–0.1525	0.1030–0.1085	87	seed	23 23	< 0.05 0.071

Report No Trial No. Doc No Year	Crop *Variety*	Country	Application			Residues		
			kg/ha (ai)	kg/hL (ai)	GS	Portion analysed	DALT (days)	Total residue prothioconazole (mg/kg)
RAJAY026 JA021-04H-P2 M-270206-01-1 2004	Soya *NKS28W2*	USA Springfield, Nebraska	0.1499–0.1504	0.1092–0.1106	80	seed	19 19	< 0.05 < 0.05
RAJAY026 JA024-04H-P2 M-270206-01-1 2004	Soya *Croplan RT0907*	USA Britton, South Dakota	0.1490–0.1491	0.159–0.159	83	seed	19 19	< 0.05 < 0.05
RAJAY026 JA025-04H-P2 M-270206-01-1 2004	Soya *Croplan RT1447*	USA Dumfries, Minnesota	0.1501–0.1508	0.0847–0.0852	79	seed	21 21	< 0.05 < 0.05
RAJAY026 JA026-04H M-270206-01-1 2004	Soya *SC 9373*	USA New Holland, Ohio	0.1506–0.1554	0.0999–0.1045	93	seed	20 20	0.142 0.103
RAJAY026 JA027-04H-P2 M-270206-01-1 2004	Soya *92M70*	USA Bagley, Iowa	0.1478–0.1512	0.1102–0.1176	79	seed	19 19	< 0.05 < 0.05
RAJAY026 JA028-04H-P2 M-270206-01-1 2004	Soya *DynaGro DG 32M32RR*	USA York, Nebraska	0.1488–0.1500	0.0798–0.0802	80	seed	19 19	< 0.05 < 0.05
RAJAY026 JA029-04H M-270206-01-1 2004	Soya *Pioneer RR*	USA Sheridan, Indiana	0.1464–0.1477	0.0940–0.0954	97	seed	21 21	< 0.05 < 0.05
RAJAY026 JA030-04H-P2 M-270206-01-1 2004	Soya *Pioneer 93M80*	USA Richland, Iowa	0.1497–0.1520	0.0927–0.1178	83	seed	21 21	< 0.05 < 0.05
RAJAY026 JA031-04H-P2 M-270206-01-1 2004	Soya *Pioneer 91M50*	USA Geneva, Minnesota	0.1496–0.1521	0.0935–0.0972	80	seed	20 20	< 0.05 < 0.05
RAJAY026 JA032-04H-P2 M-270206-01-1 2004	Soya *Pioneer 93B85*	USA Geneva, Minnesota	0.1489–0.1503	0.0877–0.0887	77	seed	21 21	< 0.05 < 0.05
RAJAY026 JA033-04H M-270206-01-1 2004	Soya *BT-383CR*	USA Carlyle, Illinois	0.1503–0.1510	0.155–0.161	79	seed	21 21	< 0.05 < 0.05
RAJAY026 JA022-04HA M-270206-01-1 2005	Soya *RG 200 RR*	USA Sabin, Minnesota	0.1481–0.1499	0.09297–0.09875	69	seed	19 19	< 0.05 < 0.05

GS growth stage

In Brazil, three foliar spray applications of 325 SC were made to soya beans at a target rate of 87.5 g prothioconazole/ha using spray volumes of 200 L/ha. The first application was made at BBCH growth stage 65 to 70. Intervals between applications were 14 days. All applications were made using ground-based equipment. A non-ionic surfactant (NIS) was added as a spray adjuvant at the lowest labelled rate. In all trials, seed samples were taken 30 days after last application.

In addition three supervised residue trials were carried out with 480 SC formulation at a rate of 150 g prothioconazole/ha using spray volumes of 200 L/ha. Intervals between applications were 15 days.

The *JAU6476-desthio* was quantified by LC/MS-MS.

Whatever the product used (325 SC or 480 SC), level of JAU6476 residue were always non detectable in soya bean seed at PHI of 30 days (data not shown).

Table 66 JAU-desthio residues in soya bean seed derived from supervised trials following applications of SC or EC formulations in Brazil

Report No Trial No. Doc No Year	Crop *Variety*	Country	Application						Residues	
			FL	No	kg/ha (ai)	kg/hL (ai)	GS	Portion analysed	DALT (days)	JAU 6476-desthio (mg/kg)
Application rate: 2×88 g ai/ha JAU6476 SC325										
UNESP RA-1056/06 BRA-FR06BRA014-P1 M-284576-01-2 2006	Soya *CD 201*	Brazil Paulinia SP	325 SC	3	0.088	0.044	71	seed	30	< 0.01
UNESP RA-1058/06 BRA-FR06BRA014-P3 M-284588-01-2 2006	Soya *BRS 245 (RR)*	Brazil Dourados MS	325 SC	3	0.088	0.044	70	seed	30	< 0.01
UNESP RA-1059/06 BRA-FR06BRA014-P4 M-284591-01-2 2006	Soya *Conquista*	Brazil Rio Verde GO	325 SC	3	0.088	0.044	74	seed	30	< 0.01
Application rate: 2×150 g ai/ha JAU6476 250EC										
UNESP RA-960/05 BRA-FR05BRA005-P1-A M-253525-01-2 2005	Soya *CD 205*	Brazil EAE-Paulinia SP	250 EC	2	0.150	0.0750	77	seed	30	< 0.01
UNESP RA-961/05 BRA-FR05BRA005-P2-A M-253528-01-2 2005	Soya *A 7002*	Brazil Rio Verde / GO	250 EC	2	0.150	0.0750	73	seed	30	< 0.01
UNESP RA-962/05 BRA-FR05BRA005-P3-A M-253529-01-2 2005	Soya *BRS 133*	Brazil Dourados MS	250 EC	2	0.150	0.0750	78	seed	30	0.01

Report No Trial No. Doc No Year	Crop *Variety*	Country	Application						Residues	
			FL	No	kg/ha (ai)	kg/hL (ai)	GS	Portion analysed	DALT (days)	JAU 6476-desthio (mg/kg)
Application rate: 2×300 g ai/ha prothioconazole *250EC*										
UNESP RA-960/05 BRA-FR05BRA005-P1-B M-253525-01-2 2005	Soya *CD 205*	Brazil EAE-Paulinia SP	250 EC	2	0.300	0.150	77	seed	30	0.03
UNESP RA-961/05 BRA-FR05BRA005-P2-B M-253528-01-2 2005	Soya *A 7002*	Brazil Rio Verde / GO	250 EC	2	0.300	0.150	73	seed	30	0.01
UNESP RA-962/05 BRA-FR05BRA005-P3-B M-253529-01-2 2005	Soya *BRS 133*	Brazil Dourados MS	250 EC	2	0.300	0.150	78	seed	30	0.02

Primary feed commodities

Description of trial conditions are given under food commodities

Table 67 Results of residue trials conducted with JAU 6476 on sugar beets in the USA

Report No Trial No. Doc No Year	Crop *Variety*	Country	Application				Residues		
			FL	No	kg/ha (ai)	kg/hL (ai)	Portion analysed	DALT (days)	Total residue JAU 6476 (mg/kg)
Decline trials									
RAJAY024 JA001-04D M-278843-01-1 2004	Sugar beet *unknown*	USA Springfield, Nebraska	480 SC	3	0.201–0.204	0.147–0.149	Tops	0 0 7 7 13 13 20 20 27 27	5.13 4.86 1.36 1.13 0.971 0.810 1.02 0.750 0.811 0.673
Harvest trials									
RAJAY024 JA002-04H M-278843-01-1 2004	Sugar beet *Tonic*	USA Sabin, Minnesota	480 SC	3	0.203–0.208	0.197–0.204	Tops	6 6 14 14	2.97 3.70 0.916 1.43
RAJAY024 JA003-04H M-278843-01-1 2004	Sugar beet *Talbot*	USA Rockwood, Ontario	480 SC	3	0.200–0.214	0.210–0.235	Tops	6 6 14 14	3.56 4.18 1.80 1.69

Report No Trial No. Doc No Year	Crop *Variety*	Country	Application				Residues		
			FL	No	kg/ha (ai)	kg/hL (ai)	Portion analysed	DALT (days)	Total residue JAU 6476 (mg/kg)
RAJAY024 JA004-04H M-278843-01-1 2004	Sugar beet *Hilleshog 2433RZ*	USA Britton, South Dakota	480 SC	3	0.199	0.212	Tops	7 7 14 14	3.48 2.96 1.84 1.46
RAJAY024 JA005-04H M-278843-01-1 2004	Sugar beet *66283 Medium*	USA Theilman, Minnesota	480 SC	3	0.201	0.177	Tops	6 6 14 14	1.90 1.61 1.53 1.64
RAJAY024 JA006-04H M-278843-01-1 2004	Sugar beet *Crystal 955*	USA Velva, North Dakota	480 SC	3	0.196–0.201	0.138–0.143	Tops	7 7 14 14	2.60 2.08 1.40 1.07
RAJAY024 JA007-04H M-278843-01-1 2004	Sugar beet *Wrangler*	USA Levelland, Texas	480 SC	3	0.202–0.208	0.136–0.140	Tops	7 7 14 14	0.521 0.391 0.290 0.200
RAJAY024 JA008-04H M-278843-01-1 2004	Sugar beet *Beta 8757 LL*	USA Jerome, Idaho	480 SC	3	0.199–0.203	0.108–0.110	Tops	7 7 14 14	0.438 0.521 0.529 0.248
RAJAY024 JA009-04H M-278843-01-1 2004	Sugar beet *Beta 4430R*	USA Porterville, California	480 SC	3	0.200–0.202	0.112–0.143	Tops	7 7 14 14	2.05 1.78 1.97 1.53
RAJAY024 JA010-04H M-278843-01-1 2004	Sugar beet *Alpine*	USA Fresno, California	480 SC	3	0.194–0.208	0.114–0.118	Tops	7 7 14 14	1.66 1.47 1.18 1.08
RAJAY024 JA011-04H M-278843-01-1 2004	Sugar beet *Beta 4490R*	USA Rupert, Idaho	480 SC	3	0.199–0.202	0.192–0.201	Tops	7 7 14 14	0.814 0.689 0.228 0.350
RAJAY024 JA012-04H M-278843-01-1 2004	Sugar beet *Beta 4490R*	USA Twin Falls, Idaho	480 SC	3	0.198–0.202	0.108–0.115	Tops	7 7 14 14	0.651 0.691 0.378 0.310

Cereals

Wheat forage and straw

Table 68 Results of wheat seed treatment residue trials conducted with prothioconazole in Europe.

Country Year	Crop *Variety*	FL[a]	Application			Portion analysed	DALT[c] [days]	Residues determined as JAU 6476-desthio [mg/kg]	Report No. Trial No. Doc No
			No	g/dt[b] ai	kg/ha ai				
Great Britain 1999	Spring Wheat *Chablis*	200 FS	1	15.0	0.030	Green material Straw	50 130	< 0.05 < 0.05	RA-2010/99 R 1999 0173/9 M-073513-01-1
Germany 1999	Spring Wheat *Thasos*	200 FS	1	15.0	0.027	Green material Straw	35 46 62 139	< 0.05 < 0.05 < 0.05 < 0.05	RA-2010/99 R 1999 0174/7 M-073513-01-1
Southern France 1999	Spring Wheat *Furio*	200 FS	1	15.0	0.030	Green material Straw	73 94 155	< 0.05 < 0.05 < 0.05	RA-2010/99 R 1999 0175/5 M-073513-01-1
Southern France 1999	Spring Wheat *Furio*	200 FS	1	15.0	0.030	Green material Straw	61 81 134	< 0.05 < 0.05 < 0.05	RA-2010/99 R 1999 0176/3 M-073513-01-1
Germany 2000	Spring Wheat *Lavett*	200 FS	1	15.0	0.030	Green material Straw	61 146	< 0.05 < 0.05	RA-2091/00 R 2000 0002/2 M-075017-01-1
Northern France 2000	Spring Wheat *Furio*	200 FS	1	15.0	0.024	Green material Straw	62 149	< 0.05 < 0.05	RA-2091/00 R 2000 0424/9 M-075017-01-1
Southern France 2000	Spring Wheat *Furio*	200 FS	1	15.0	0.023	Green material Straw	70 146	< 0.05 < 0.05	RA-2090/00 R 2000 0003/0 M-073003-01-1
Italy 2000	Spring Wheat *Pandas*	200 FS	1	15.0	0.030	Green material Straw	54 120	< 0.05 < 0.05	RA-2090/00 R 2000 0423/0 M-073003-01-1

[a] FS 200 is a flowable concentrate for seed treatment, containing 200 g/L prothioconazole

[b] dt = 100 kg (of seed)

[c] Days after last treatment

Table 69 Results of residue trials conducted on prothioconazole on wheat in Northern Europe: seed treatment + spraying

Country Year	Crop *Variety*	FL[a]	Application			Portion	DALT[b]	Residues determined as JAU 6476-desthio [mg/kg]	Report No. Trial No. Doc No
			No	kg/ha ai	kg/hL ai	analysed	[days]		
Germany 1999	Spring Wheat *Thasos*	200 FS 250 EC	1 3	0.027 0.200	 0.0668	Green Material Ear Rest of plant Straw	–26 0[c] 0 7 14 21 28 0[c] 0 7 14 21 28 35 < 51	< 0.05 < 0.01 0.96 0.57 0.19 0.07 0.04 0.21 1.6 <u>1.1</u> 0.36 0.23 0.16 0.14 <u>0.20</u>	RA-2003/99 R 1999 0266/2 M-075134-01-1
Germany 1998	Winter Wheat *Bandit*	200 FS 250 EC	1 3	0.027 0.200	 0.0668	Green Material Ear Rest of plant Straw	–39 0 21 28 0 21 28 35 < 50	< 0.05 0.78 0.05 0.03 1.2 0.16 0.13 0.25 <u>0.31</u>	RA-2003/99 R 1999 0023/6 M-075134-01-1
Germany 1998	Winter Wheat *Bandit*	200 FS 250 EC	1 3	0.027 0.200	 0.0668	Green Material Ear Rest of plant Straw	–36 0 21 28 0 21 28 35 < 46	< 0.05 0.79 0.07 0.04 1.2 0.46 0.40 0.67 <u>0.72</u>	RA-2003/99 R 1999 0025/2 0025-99
France 1998	Winter Wheat *Sideral*	200 FS 250 EC	1 3	0.027 0.200	 0.0668	Green Material Ear Rest of plant Straw	–38 0 21 28 0 21 28 35 < 43	< 0.05 0.59 0.02 0.02 0.60 0.09 0.13 <u>0.11</u> 0.11	RA-2003/99 R 1999 0026/0 0026-99

Country Year	Crop *Variety*	FL[a]	Application			Portion	DALT[b]	Residues determined as JAU 6476-desthio [mg/kg]	Report No. Trial No. Doc No
			No	kg/ha ai	kg/hL ai	analysed	[days]		
Great Britain 1999	Winter Wheat *Abbot*	250 EC	3	0.200	0.0668	Ear Rest of plant Straw	0[c] 0 21 28 35 << 0[c] 0 21 28 35 << 54	< 0.01 1.2 0.07 0.02 0.02 0.19 1.8 0.21 0.14 0.14 <u>0.19</u>	RA-2003/99 R 1999 0027/9 0027-99
Germany 2000	Spring Wheat *Vinjett*	250 EC	3	0.200	0.0668	Ear Rest of plant Straw	0[c] 0 7 14 35 << 0[c] 0 7 14 35 << 64	0.06 1.6 0.52 0.18 0.05 0.18 0.89 <u>0.32</u> 0.23 0.25 <u>0.14</u>	RA-2104/00 R 2000 0454/0 M-088723-01-1
Germany 2000	Spring Wheat *Lavett*	250 EC	3	0.200	0.0668	Ear Rest of plant Straw	0[c] 0 7 14 35 << 0[c] 0 7 14 35 << 58	< 0.01 1.4 0.40 0.18 0.03 0.19 1.6 <u>0.57</u> 0.20 0.08 <u>0.09</u>	RA-2104/00 R 2000 0457/5 M-088723-01-1
France 2000	Spring Wheat *Furio*	250 EC	3	0.200	0.0668	Ear Rest of plant Straw	0[c] 0 7 14 0[c] 0 7 14 35 << 42	< 0.01 0.79 0.09 0.06 < 0.05 1.5 <u>0.11</u> 0.12 0.07 <u>0.08</u>	RA-2104/00 R 2000 0474/5 M-088723-01-1

Country Year	Crop *Variety*	FL[a]	Application			Portion	DALT[b]	Residues determined as JAU 6476-desthio [mg/kg]	Report No. Trial No. Doc No
			No	kg/ha ai	kg/hL ai	analysed	[days]		
Great Britain 2000	Spring Wheat *Chablis*	250 EC	3	0.200	0.0668	Ear	0[c]	< 0.01	RA-2104/00 R 2000 0475/3 M-088723-01-1
							0	0.80	
							7	0.26	
							14	0.07	
							35 <<	0.02	
						Rest of plant	0[c]	0.74	
							0	2.4	
							7	1.0	
							14	0.5	
							35 <<	0.32	
						Straw	56	0.27	
Germany 2000	Spring Wheat *Lavett*	250 EC	3	0.200	0.0668	Ear	0[c]	< 0.01	RA-2104/00 R 2000 0476/1 M-088723-01-1
							0	0.86	
							6	0.99	
							14	0.32	
							35 <<	0.05	
						Rest of plant	0[c]	0.17	
							0	1.6	
							6	1.8	
							14	0.72	
							35 <<	0.11	
						Straw	49	0.15	

[a] 250 EC is an emulsifiable concentrate formulation, containing 250 g/L prothioconazole

[b] Days after last treatment

[c] Prior to last treatment

Table 70 Results of residue trials conducted on prothioconazole on wheat in Southern Europe, seed treatment + spraying

Country Year	Crop *Variety*	FL[a]	Application			Portion analysed	DALT[b] [days]	Residues determined as JAU 6476-desthio [mg/kg]	Report No. Trial No Doc No
			No.	kg/ha as	kg/hL as				
France 1998	Winter Wheat *Sideral*	200 FS	1	0.027		Green Material	–53	< 0.05	RA-2149/98 R 1998 1586/1 M-083957-01-1
		250 EC	3	0.169	0.0668	Ear	0	0.56	
				0.200	0.0668		21	0.05	
							28	0.07	
						Rest of plant	0	0.87	
							21	0.41	
							28	0.47	
						Straw	35 <<	0.51	
							40	0.72	

Country Year	Crop *Variety*	FL[a]	Application			Portion analysed	DALT[b] [days]	Residues determined as JAU 6476-desthio [mg/kg]	Report No. Trial No Doc No
			No.	kg/ha as	kg/hL as				
Spain 1998	Winter Wheat *Adalid*	200 FS 250 EC	1 3	0.023 0.200	 0.0668	Green Material Ear Rest of plant Straw	–50 0 20 0 20 28 34 48	< 0.05 1.4 0.20 3.3 0.74 0.89 <u>1.0</u> 0.85	RA-2149/98 R 1998 1588/8 M-083957-01-1
Italy 1998	Winter Wheat *MEC*	200 FS 250 EC	1 3	0.024 0.200	 0.0668	Green Material Ear Rest of plant Straw	–45 0 21 0 21 28 35 42	< 0.05 0.68 0.06 1.5 0.87 0.45 0.31 <u>0.52</u>	RA-2149/98 R 1998 1589/6 M-083957-01-1
France 1998	Winter Wheat *Sideral*	200 FS 250 EC	1 3	0.027 0.200	 0.0668	Green Material Ear Rest of plant Straw	–54 0 21 28 0 21 28 34 << 50	< 0.05 1.0 0.13 0.12 1.4 0.72 0.84 <u>0.47</u> 0.41	RA-2149/98 R 1998 1314/1 M-083957-01-1
Spain 1998	Winter Wheat *Soisson*	200 FS 250 EC	1 3	0.022 0.200	 0.0668	Green Material Ear Rest of plant Straw	–50 0 20 0 20 28 34 << 48	< 0.05 1.4 0.06 2.0 0.48 0.63 <u>0.72</u> 0.66	RA-2149/98 R 1998 1725/2 M-083957-01-1
Spain 2000	Winter Wheat *Sarina*	250 EC	3	0.211 0.200	0.0668 0.0668	Ear Rest of plant Straw	0[c] 0 6 14 0[c] 0 6 14 35 << 42	< 0.01 1.3 0.48 0.14 0.14 1.7 <u>0.89</u> 0.35 <u>0.25</u> 0.22	RA-2105/00 R 2000 0455/9 M-088975-01-1

Country Year	Crop *Variety*	FL[a]	Application			Portion analysed	DALT[b] [days]	Residues determined as JAU 6476-desthio [mg/kg]	Report No. Trial No Doc No
			No.	kg/ha as	kg/hL as				
France 2000	Triticale *Magistral*	250 EC	3	0.200	0.0668	Ear Rest of plant Straw 	0[c] 0 7 14 0[c] 0 7 14 35 57	< 0.01 1.8 0.62 0.18 0.30 1.3 <u>0.65</u> 0.29 0.26 <u>0.53</u>	RA-2105/00 R 2000 0478/8 M-088975-01-1
France 2000	Durum Wheat *Orjaune*	250 EC	3	0.200	0.0668	Ear Rest of plant Straw 	0[c] 0 7 14 0[c] 0 7 14 35 49	0.01 1.7 0.48 0.18 0.22 1.6 <u>0.92</u> 0.45 0.31 <u>0.42</u>	RA-2105/00 R 2000 479/6 M-088975-01-1
Spain 2000	Winter Wheat *Soissons*	250 EC	3	0.200	0.0668	Ear Rest of plant Straw 	0[c] 0 7 15 0[c] 0 7 15 36 << 42	0.04 1.2 0.44 0.13 0.42 1.7 <u>0.78</u> 0.52 0.62 <u>0.77</u>	RA-2105/00 R 2000 0482/6 M-088975-01-1

[a] 250 EC is an emulsifiable concentrate formulation, containing 250 g/L prothioconazole

[b] Days after last treatment

[c] Prior to last treatment

Table 71 Results of decline residue trials conducted with prothioconazole on wheat in the USA and Canada

Report No Trial No. Doc No Year	Crop *Variety*	Country	Application				Residues		
			FL	No	kg/ha (ai)	kg/hL (ai)	Portion analysed	DALT (days)	total residue prothioconazole (mg/kg)
200524 J6046-00D M-001538-01-1 2000	Wheat *Russ*	USA New Rockford, North Dakota	480 SC	2	0.124–0.198	0.0445 – 0.0734	forage	0 0 1 1 7 7 14 14	7.465 7.234 3.358 3.035 0.233 0.263 < 0.1 < 0.1

Report No Trial No. Doc No Year	Crop *Variety*	Country	Application				Residues		
			FL	No	kg/ha (ai)	kg/hL (ai)	Portion analysed	DALT (days)	total residue prothioconazole (mg/kg)
					0.123–0.203	0.0438 – 0.0720	hay	6 6 14 14 20 20 28 28	3.096 3.088 0.898 0.675 0.306 0.569 0.601 0.325
							straw	36 36 40 40 46 46 50 50	0.661 0.389 0.352 0.327 0.493 n.a. 0.309 0.480
200524 J6045-00D M-001538-01-1 2001	Wheat *Arapahoe*	USA Louisville Nebraska	480 SC	2	0.127–0.202	0.0765 –0.123	forage	0 0 1 1 7 7 14 14	12.295 7.649 8.212 8.046 1.827 1.383 0.273 0.325
					0.127–0.202	0.0778 –0.126	hay	7 7 14 14 21 21 28 28	0.774 0.637 0.417 0.482 0.219 0.191 0.102 < 0.1
							straw	35 35 39 39 44 44 49 49	0.251 0.210 0.182 0.209 0.253 0.196 0.209 0.231

Table 72 Results of residue trials conducted with prothioconazole on wheat in the USA and Canada

Report No Trial No. Doc No Year	Crop *Variety*	Country	Application				Residues		
			FL	No	kg/ha (ai)	kg/hL (ai)	Portion analysed	DALT (days)	total residue prothioconazole (mg/kg)
Harvest trials for forage									
200524 J6169-00H M-001538-01-1 2003	Wheat, winter *Pioneer 2684*	USA Tifton, Georgia	480 SC	2	0.127–0.202	0.121–0.149	forage	7 7	0.547 0.383

Report No Trial No. Doc No Year	Crop *Variety*	Country	Application				Residues		
			FL	No	kg/ha (ai)	kg/hL (ai)	Portion analysed	DALT (days)	total residue prothioconazole (mg/kg)
200524 J6170-00H M-001538-01-1 2003	Wheat, winter *Pioneer 2684*	USA Leland, Mississippi	480 SC	2	0.128–0.207	0.0803–0.122	forage	7 7	2.528 2.864
200524 J6171-00H M-001538-01-1 2003	Wheat, winter *Jagger*	USA Stilwell, Kansas	480 SC	2	0.124–0.198	0.0869–0.164	forage	7 7	0.307 0.366
200524 J6172-00H M-001538-01-1 2003	Wheat, winter *Wahoo 14 W3-43*	USA Louisville, Nebraska	480 SC	2	0.127–0.202	0.0752–0.137	forage	7 7	1.112 1.161
200524 J6173-00H M-001538-01-1 2002	Wheat, winter *Ogallala*	USA Uvalde, Texas	480 SC	2	0.124–0.204	0.0773–0.0936	forage	7 7	6.987 4.696
200524 J6174-00H M-001538-01-1 2002	Wheat, spring *Alsen*	USA New Rockford, North Dakota	480 SC	2	0.128–0.201	0.0452–0.0717	forage	7 7	0.425 0.365
200524 J6175-00H M-001538-01-1 2002	Wheat, spring *Alsen*	USA Eldridge, North Dakota	480 SC	2	0.126–0.210	0.0449–0.0723	forage	7 7	0.105 0.119
200524 J6176-00H M-001538-01-1 2002	Wheat, spring *Ingot*	USA Leola, South Dakota	480 SC	2	0.128–0.203	0.0910–0.145	forage	7 7	< 0.1 < 0.1
200524 J6177-00H M-001538-01-1 2002	Wheat, spring *CDC Teal*	Canada Dundum, Saskatchewan America, North	480 SC	2	0.124–0.198	0.115–0.183	forage	7 7	2.338 2.941
200524 J6178-00H M-001538-01-1 2002	Wheat, spring *A.C. Barrie*	Canada Taber, Alberta	480 SC	2	0.126–0.208	0.127–0.201	forage	7 7	1.413 1.792
200524 J6179-00H M-001538-01-1 2003	Wheat, winter *Tam 105*	USA Levelland Texas	480 SC	2	0.127–0.199	0.0667–0.108	forage	7 7	1.461 1.749
200524 J6180-00H M-001538-01-1 2003	Wheat, winter *Jagger*	USA Hart, Texas	480 SC	2	0.127–0.203	0.0716–0.112	forage	7 7	1.883 1.325

Report No Trial No. Doc No Year	Crop *Variety*	Country	Application				Residues		
			FL	No	kg/ha (ai)	kg/hL (ai)	Portion analysed	DALT (days)	total residue prothioconazole (mg/kg)
200524 J6181-00H M-001538-01-1 2003	Wheat, winter *Tam 105*	USA Wolforth, Texas	480 SC	2	0.126–0.204	0.0661–0.109	forage	7 7	2.294 2.321
200524 J6182-00H M-001538-01-1 2003	Wheat, winter *Coker 9663*	USA Colony, Oklahoma	480 SC	2	0.129–0.197	0.0998–0.160	forage	7 7	1.296 1.448
200524 J6183-00H M-001538-01-1 2002	Wheat, spring *Pennewawa*	USA Hood River, Oregon	480 SC	2	0.123–0.204	0.0630–0.0991	forage	7 7	0.948 0.794
200524 J6184-00H M-001538-01-1 2002	Wheat, spring *AC Barrie*	USA Minto, Manitoba America, North	480 SC	2	0.124–0.201	0.0831–0.132	forage	7 7	0.136 0.143
200524 J6185-00H M-001538-01-1 2002	Wheat, spring *Prodigy*	Canada Rosthern, Saskatchewan	480 SC	2	0.126–0.198	0.116–0.181	forage	7 7	0.727 0.802
200524 J6186-00H M-001538-01-1 2002	Wheat, spring *AC Splender*	Canada Edmonton, Alberta	480 SC	2	0.126–0.201	0.120–0.185	forage	7 7	1.529 1.222
200524 J6187-00H M-001538-01-1 2002	Wheat, spring *AC Splender*	Canada Spruce Grove, Alberta	480 SC	2	0.122–0.199	0.112–0.190	forage	7 7	1.420 1.378
200524 J6188-00H M-001538-01-1 2002	Wheat, spring *AC Cora*	Canada Brookdale, Manitoba	480 SC	2	0.123–0.199	0.113–0.119	forage	7 7	1.532 2.061
200524 J6189-00H M-001538-01-1 2002	Wheat, spring *AC Cora*	Canada Bethany, Manitoba	480 SC	2	0.127–0.194	0.113–0.118	forage	7 7	1.944 1.702
Harvest trials for hay, grain and straw									
200524 J6044-00H M-001538-01-1 2000	Wheat *Tahoe*	Canada St. George, Ontario	480 SC	2	0.1350–0.2110	0.0614–0.1005	hay	17 17	0.322 0.288
							straw	42 42	0.231 0.174

Report No Trial No. Doc No Year	Crop *Variety*	Country	Application				Residues		
			FL	No	kg/ha (ai)	kg/hL (ai)	Portion analysed	DALT (days)	total residue prothioconazole (mg/kg)
200524 J6047-00H M-001538-01-1 2000	Wheat *Penawawa*	USA Hermiston, Oregon	480 SC	2	0.129–0.206	0.0446–0.0706	hay	13 13	0.374 0.339
							straw	42 42	0.136 0.113
200524 J6048-00H M-001538-01-1 2001	Wheat *Ogallala*	USA Uvalde, Texas	480 SC	2	0.130–0.196	0.0691–0.116	hay	14 14	2.998 3.182
							straw	42 42	0.846 0.731
200524 J6049-00H M-001538-01-1 2001	Wheat *Jagger*	USA Claude, Texas	480 SC	2	0.128–0.207	0.0647–0.103	hay	14 14	0.612 0.668
							straw	41 41	0.307 0.328
200524 J6050-00H M-001538-01-1 2001	Wheat *Custer*	USA Cordell, Oklahoma	480 SC	2	0.123–0.203	0.0991–0.158	hay	14 14	1.660 1.252
							straw	38 38	0.615 0.767
200524 J6051-00H M-001538-01-1 2001	Wheat *Custer*	USA Frederick, Oklahoma	480 SC	2	0.120–0.198	0.0644–0.102	hay	14 14	0.432 0.490
							straw	10 10	0.650 n.a.
200524 J6052-00H M-001538-01-1 2001	Wheat *Tam 200*	USA Hart, Texas America, North	480 SC	2	0.127–0.201	0.0836–0.135	hay	13 13	1.928 1.889
							straw	35 35	1.643 1.359
200524 J6053-00H M-001538-01-1 2000	Wheat *2375*	USA Velva, North Dakota	480 SC	2	0.128–0.201	0.0454–0.0720	hay	13 13	0.322 0.401
							straw	33 33	0.106 0.151

Report No Trial No. Doc No Year	Crop *Variety*	Country	Application				Residues		
			FL	No	kg/ha (ai)	kg/hL (ai)	Portion analysed	DALT (days)	total residue prothioconazole (mg/kg)
200524 J6054-00H M-001538-01-1 2001	Wheat *Tam 202, Lot Star 10*	USA Levelland, Texas	480 SC	2	0.127–0.202	0.0670–0.107	hay	13 13	2.568 2.055
							straw	43 43	1.854 0.305
200524 J6055-00H M-001538-01-1 2000	Wheat *Alsen*	USA Ellendale, North Dakota	480 SC	2	0.126–0.202	0.0678–0.108	hay	12 12	0.580 0.545
							straw	39 39	0.217 0.181
200524 J6056-00H M-001538-01-1 2000	Wheat *Forge spring wheat*	USA Lake Andes, South Dakota	480 SC	2	0.126–0.201	0.0710–0.112	hay	13 13	3.569 2.442
							straw	46 46	n.a. 1.379
200524 J6057-00H M-001538-01-1 2000	Wheat *Tahoe*	Canada Paris, Ontario	480 SC	2	0.1440–0.2000	0.06122–0.1005	hay	17 17	0.463 0.447
							straw	42 42	0.261 0.264
200524 J6058-00H M-001538-01-1 2001	Wheat *Mit*	USA East Bernard, Texas	480 SC	2	0.126–0.196	0.0900–0.138	hay	12 12	0.710 1.063
							straw	32 32	0.930 1.053
200524 J6059-00H M-001538-01-1 2001	Wheat *Karl 92*	USA Stilwell, Kansas	480 SC	2	0.129–0.202	0.0679–0.106	hay	16 16	0.612 0.344
							straw	42 42	0.286 0.251
200524 J6060-00H M-001538-01-1 2001	Wheat *Becks 107*	USA Oxford, Indiana America, North	480 SC	2	0.130–0.203	0.0933–0.147	hay	14 14	0.567 0.638
							straw	43 43	0.214 0.217
200524 J6061-00H M-001538-01-1 2000	Wheat *Barrie*	Canada Red Deer, Alberta	480 SC	2	0.1260–0.2110	0.0431–0.0703	hay	14 14	0.350 0.341
							straw	57 57	0.178 0.168
200524 J6062-00H M-001538-01-1 2000	Wheat *HRS wheat prodigy*	Canada Monarch, Alberta	480 SC	2	0.1270–0.2020	0.0315–0.0514	hay	14 14	2.509 1.822
							straw	30 30	0.485 0.393

Report No Trial No. Doc No Year	Crop *Variety*	Country	Application				Residues		
			FL	No	kg/ha (ai)	kg/hL (ai)	Portion analysed	DALT (days)	total residue prothioconazole (mg/kg)
00524 J6063-00H M-001538-01-1 2001	Wheat *Pioneer 2684*	USA Benoit, Mississippi	480 SC	2	0.123–0.205	0.0794–0.120	hay	13 13	1.761 1.470
							straw	42 42	0.629 0.511
200524 J6064-00H M-001538-01-1 2001	Wheat *Cooker 107*	USA Knightdale, North Carolina	480 SC	2	0.126–0.199	0.0395–0.0622	hay	14 14	1.928 2.501
							straw	37 37	1.284 1.548
200524 J6066-00H M-001538-01-1 2000	Wheat *AC Cora*	Canada Minto, Manitoba	480 SC	2	0.1330–0.2100	0.0317–0.0506	hay	14 14	1.489 1.500
							straw	47 47	0.313 0.328
200524 J6067-00H M-001538-01-1 2000	Wheat *AC Cora*	Canada Minto, Manitoba	480 SC	2	0.1319–0.2070	0.0319–0.0504	hay	14 14	3.571 3.515
							straw	49 49	0.858 0.804
200524 J6068-00H M-001538-01-1 2000	Wheat *AC Barrie*	Canada Wakaw, Saskatchewan	480 SC	2	0.1290–0.1970	0.1181–0.1826	hay	12 12	3.305 2.866
							straw	55 55	0.789 0.663
200524 J6069-00H M-001538-01-1 2000	Wheat *McKenzie*	Canada Leask, Saskatchewan	480 SC	2	0.1250–0.2010	0.0317–0.0508	hay	12 12	1.420 1.632
							straw	48 48	0.495 0.483
200524 J6070-00H M-001538-01-1 2000	Wheat *AC Cadillac*	Canada Rostern, Saskatchewan	480 SC	2	0.1260–0.1950	0.0317–0.0504	hay	14 14	0.981 0.809
							straw	53 53	0.244 0.233
200524 J6071-00H M-001538-01-1 2000	Wheat *Barrie (certified)*	Canada Brookdale, Manitoba	480 SC	2	0.1280–0.2040	0.1141–0.1835	hay	14 14	3.149 2.601
							straw	43 43	0.228 0.282
200524 J6072-00H M-001538-01-1 2000	Wheat *Barrie*	Canada Lacombe, Alberta	480 SC	2	0.1260–0.2010	0.0424–0.0674	hay	14 14	1.142 1.080
							straw	57 57	0.347 0.322

Report No Trial No. Doc No Year	Crop *Variety*	Country	Application				Residues		
			FL	No	kg/ha (ai)	kg/hL (ai)	Portion analysed	DALT (days)	total residue prothioconazole (mg/kg)
200524 J6073-00H M-001538-01-1 2000	Wheat *AC Barrie*	Canada Delisle, Saskatchewan	480 SC	2	0.1270–0.2000	0.0318–0.0504	hay	15 15	0.995 0.821
							straw	38 38	0.311 0.311
200524 J6074-00H M-001538-01-1 2000	Wheat *Prodigy*	Canada Delisle, Saskatchewan	480 SC	2	0.1260–0.2000	0.0316–0.0510	hay	15 15	1.431 1.693
							straw	43 43	0.575 0.633
200524 J6075-00H M-001538-01-1 2000	Wheat *HRS wheat prodigy*	Canada Warner, Alberta	480 SC	2	0.1240–0.2050	0.0315–0.0504	hay	14 14	2.287 1.308
							straw	31 31	1.838 1.960
200524 J6076-00H M-001538-01-1 2000	Wheat *Prodigy*	Canada Coaldale, Alberta	480 SC	2	0.1250–0.1980	0.0318–0.0498	hay	14 14	1.886 1.286
							straw	35 35	1.052 1.058
200524 J6077-00H M-001538-01-1 2000	Wheat *Prodigy*	Canada Kipp, Alberta	480 SC	2	0.1260–0.2000	0.0315–0.0507	hay	14 14	1.641 2.428
							straw	30 30	0.443 0.515

Barley forage and straw

Table 73 Results of residue trials conducted on prothioconazole on barley in Northern Europe

Country Year	Crop *Variety*	FL[a]	Application			Portion analysed	DALT[b] [days]	Residues JAU 6476-desthio [mg/kg]	Report No. Trial No. Doc No
			No	kg/ha ai.	kg/hL ai				
Germany 1998	Spring Barley *Scarlett*	200FS 250EC	2	0.200 0.400	0.0668 0.1333	Ear Rest of plant Straw	0 36 << 0 36 << 57	4.3 0.03 3.2 0.15 <u>0.24</u>	RA-2150/98 R 1998 1256/0 M-073128-02-1
Germany 1998	Spring Barley *Scarlett*	200FS 250EC	2	0.200	0.0668	Green Material Ear Rest of plant Straw	–4 0 36 << 0 36 << 59	< 0.05 1.8 < 0.01 3.2 0.06 <u>0.14</u>	RA-2140/98 R 1998 1580/2 M-073128-02-1

Country Year	Crop *Variety*	FL[a]	Application			Portion analysed	DALT[b] [days]	Residues JAU 6476-desthio [mg/kg]	Report No. Trial No. Doc No
			No	kg/ha ai.	kg/hL ai				
Germany 1998	Spring Barley *Scarlett*	200FS 250EC	2	0.200	0.0668	Green Material Ear Rest of plant Straw	–12 0 36 << 0 36 << 57	< 0.05 2.2 0.01 2.7 0.08 <u>0.13</u>	RA-2140/98 R 1998 1247/1 M-073128-02-1
France 1998	Spring Barley *Prisma*	200FS 250EC	2	0.200	0.0715	Green Material Ear Rest of plant Straw	–16 0 35 << 0 35 << 48	< 0.05 2.6 0.01 2.2 0.07 <u>0.13</u>	RA-2140/98 R 1998 1581/0 M-072786-02-1
Great Britain 1998	Spring Barley *Alexis*	200FS 250EC	2	0.200	0.0668	Green Material Ear Rest of plant Straw	–19 0 35 << 0 35 << 51	< 0.05 3.3 0.01 2.3 0.07 <u>0.10</u>	RA-2140/98 R 1998 1582/9 M-072786-02-1
Sweden 2000	Spring Barley *Henni*	250EC	2	0.200	0.0668	Ear Rest of plant Straw	0[c] 0 7 14 0[c] 0 7 14 49 35<< 49	0.01 3.2 0.86 0.12 0.33 1.3 <u>0.60</u> 0.33 0.01 0.12 <u>0.14</u>	RA-2101/00 R 2000 0452/4 M-072786-02-1
France 2000	Spring Barley *Nevada*	250EC	2	0.200	0.0668	Ear Rest of plant Straw	0[c] 0 7 14 35 << 0[c] 0 7 14 35 << 56	< 0.01 2.2 0.26 0.13 0.01 0.44 1.7 <u>1.2</u> 0.82 0.10 <u>0.10</u>	RA-2101/00 R 2000 0462/1 M-086237-01-1

Country Year	Crop *Variety*	FL[a]	Application			Portion analysed	DALT[b] [days]	Residues JAU 6476-desthio [mg/kg]	Report No. Trial No. Doc No
			No	kg/ha ai.	kg/hL ai				
Great Britain 2000	Spring Barley *Optic*	250EC	2	0.200	0.0668	Ear Rest of plant Straw	0[c] 0 7 15 35 << 0[c] 0 7 15 35 << 57	0.02 2.0 0.74 0.17 0.02 0.66 2.5 <u>2.0</u> 0.75 0.26 <u>0.30</u>	RA-2101/00 R 2000 0464/8 M-086237-01-1
Germany 2000	Spring Barley *Alexis*	250EC	2	0.200	0.0668	Ear Rest of plant Straw	0[c] 0 7 14 34 << 0[c] 0 7 14 34 << 55	0.02 1.5 0.41 0.09 0.02 0.16 1.9 <u>1.7</u> 1.2 0.28 <u>0.08</u>	RA-2101/00 R 2000 0465/6 M-086237-01-1

[a] 200 FS is a flowable concentrate for seed treatment, containing 200 g/L prothioconazole, 250 EC is an emulsifiable concentrate formulation, containing 250 g/L prothioconazole

[b] Days after last treatment

[c] Prior to last treatment

Table 74 Results of residue trials conducted on prothioconazole on barley in Southern Europe

Country Year	Crop *Variety*	FL[a]	Application			Portion analysed	DALT[b] [days]	Residues JAU 6476-desthio [mg/kg]	Report No. Trial No. Doc No.
			No.	kg/ha ai	kg/hL ai				
France 1998	Spring Barley *Volga*	200 FS 250 EC	2	0.200	0.0668	Green Material Ear Rest of plant Straw	–21 0 0 35 << 48	< 0.05 2.3 2.7 <u>1.2</u> 0.42	RA-2079/98 R 1998 1249/8 M-075011-01-1
France 1998	Winter Barley *Vertige*	250 EC	2	0.200	0.0668	Ear Rest of plant Straw	0[c] 0 21 35 << 0[c] 0 21 35 << 48	0.02 3.5 0.11 0.07 0.83 1.6 0.99 0.74 <u>1.1</u>	RA-2144/98 R 1998 1317/6 M-072984-02-1

Country Year	Crop *Variety*	FL[a]	Application			Portion analysed	DALT[b] [days]	Residues JAU 6476-desthio [mg/kg]	Report No. Trial No. Doc No.
			No.	kg/ha ai	kg/hL ai				
France 1998	Winter Barley *Pilastro*	250 EC	2	0.200	0.0668	Green Material Ear Rest of plant Straw	0[c] 0 21 21 35 << 41	0.07 2.6 0.04 0.23 <u>0.19</u> 0.19	RA-2144/98 R 1998 1571/3 M-072984-02-1
France 1998	Winter Barley *Carina*	250 EC	2	0.200	0.0668	Green Material Ear Rest of plant Straw	0[c] 0 21 35 << 21 35 << 57	0.05 1.9 0.05 0.01 0.25 0.05 <u>0.16</u>	RA-2144/98 R 1998 1572/1 M-072984-02-1
Spain 2000	Spring Barley *Graphic*	250 EC	2	0.217 0.200	0.0668 0.0668	Ear Rest of plant Straw	0[c] 0 6 13 0[c] 0 6 13 35 << 41	0.01 1.9 0.57 0.14 0.28 0.98 <u>1.0</u> 0.53 <u>0.38</u> 0.32	RA-2103/00 R 2000 0453/2 M-086807-01-1
Italy 2000	Spring Barley *Patty*	250 EC	2	0.200	0.0668	Ear Rest of plant Straw	0[c] 0 7 14 0[c] 0 7 14 35<< 49	< 0.01 1.8 0.77 0.26 0.42 2.4 <u>2.6</u> 1.8 <u>1.1</u> 1.1	RA-2103/00 R 2000 0470/2 M-086807-01-1
France 2000	Spring Barley *Nevada*	250 EC	2	0.200	0.0668	Ear Rest of plant Straw	0[c] 0 7 14 0[c] 0 7 14 35 << 42	0.01 1.3 0.19 0.06 0.10 2.1 <u>0.85</u> 0.38 0.41 <u>0.53</u>	RA-2103/00 R 2000 0472/9 M-086807-01-1

Country Year	Crop *Variety*	FL[a]	Application			Portion analysed	DALT[b] [days]	Residues JAU 6476-desthio [mg/kg]	Report No. Trial No. Doc No.
			No.	kg/ha ai	kg/hL ai				
France 2000	Spring Barley *Nevada*	250 EC	2	0.200	0.0668	Ear Rest of plant Straw	0[c] 0 7 15 0[c] 0 7 15 35 < 52	0.01 2.4 0.33 0.07 0.84 2.6 <u>1.7</u> 0.80 <u>0.75</u> 0.24	RA-2103/00 R 2000 0473/7 M-086807-01-1

[a] 200 FS is a flowable concentrate for seed treatment, containing 200 g/L prothioconazole, 250 EC is an emulsifiable concentrate formulation, containing 250 g/L prothioconazole

[b] Days after last treatment;

[c] Prior to last treatment

Table 75 Results of residue trials conducted with prothioconazole on barley in the USA and Canada

Report No Trial No. Doc No Year	Crop *Variety*	Country	Application				Residues		
			FL	No	kg/ha (ai)	kg/hL (ai)	Portion analysed	DALT (days)	Total residue prothioconazole (mg/kg)
200806 J6001-00D M-000715-01-1 2000	Barley *Robust*	USA Northwood North Dakota	480SC	2	0.131–0.198	0.0467–0.0702	hay	8 8 13 13 22 22 28 28	0.741 0.831 0.647 0.731 0.610 0.523 0.782 0.561
							straw	32 32 37 37 44 44 47 47	0.193 0.180 0.225 0.188 0.075 0.096 0.102 0.112

Report No Trial No. Doc No Year	Crop *Variety*	Country	Application				Residues		
			FL	No	kg/ha (ai)	kg/hL (ai)	Portion analysed	DALT (days)	Total residue prothioconazole (mg/kg)
200806 J6008-00D M-000715-01-1 2000	Barley *Chapais*	Canada Branchton, Ontario	480SC	2	0.1280–0.2020	0.0621–0.0973	hay	9 9 14 14 21 21 29 29	0.966 0.627 0.734 0.317 0.211 0.167 0.147 0.199
							straw	36 36 39 39 45 45 49 49	0.128 0.211 0.217 0.177 0.151 0.155 0.159 0.147
Harvest trials									
200806 J6002-00H M-000715-01-1 2000	Barley *Steptoe*	USA Hermiston Oregon	480SC	2	0.124–0.206	0.0460–0.0700	hay	13 13	0.358 0.318
							straw	42 42	0.051 1.011
200806 J6003-00H M-000715-01-1 2001	Barley *Baretta*	USA Maricopa, Arizona	480SC	2	0.131–0.206	0.0461–0.0732	hay	14 14	1.814 1.741
							straw	48 48	1.336 1.321
200806 J6004-00H M-000715-01-1 2001	Barley *Baretta*	USA Wilcox, Arizona	480SC	2	0.126–0.195	0.0452–0.0724	hay	15 15	2.577 1.669
							straw	71 71	1.324 1.269
200806 J6005-00H M-000715-01-1 2000	Barley *Robust*	USA Velva, North Dakota	480SC	2	0.128–0.203	0.0455–0.0723	hay	13 13	0.758 0.668
							straw	33 33	0.083 0.100
200806 J6006-00H M-000715-01-1 2000	Barley *Robust*	USA New Rockford, North Dakota	480SC	2	0.126–0.212	0.0444–0.0750	hay	14 14	0.829 0.656
							straw	36 36	0.209 0.313
200806 J6007-00H M-000715-01-1 2000	Barley *Robust*	USA Ellendale, North Dakota	480SC	2	0.128–0.202	0.0676–0.107	hay	14 14	0.578 0.551
							straw	43 43	< 0.05 0.053
200806 J6009-00H M-000715-01-1 2000	Barley *Morex*	USA Jerome, Idaho	480SC	2	0.126–0.204	0.0452–0.0727	hay	12 12	0.462 0.438
							straw	43 43	0.052 0.065

Report No Trial No. Doc No Year	Crop *Variety*	Country	Application				Residues		
			FL	No	kg/ha (ai)	kg/hL (ai)	Portion analysed	DALT (days)	Total residue prothioconazole (mg/kg)
200806 J6010-00H M-000715-01-1 2000	Barley *Robust*	USA Northwood, North Dakota	480SC	2	0.126–0.201	0.0450–0.0715	hay	14 14	0.556 0.767
							straw	44 44	0.085 0.109
200806 J6013-00H M-000715-01-1 2000	Barley *AC Stephen*	USA Germans-ville, Pennsylvania	480SC	2	0.131–0.197	0.0384–0.0653	hay	13 13	1.191 1.235
							straw	57 57	0.185 0.199
200806 J6078-00H M-000715-01-1 2000	Barley *Robust*	Canada Minto, Manitoba	480SC	2	0.1260–0.2060	0.0319–0.0507	hay	13 13	6.590 5.305
							straw	36 36	0.711 0.932
200806 J6079-00H M-000715-01-1 2000	Barley *Robust*	Canada Minto, Manitoba America, North	480SC	2	0.1280–0.1940	0.0321–0.0508	hay	16 16	1.796 3.895
							straw	32 32	1.828 1.282
200806 J6080-00H M-000715-01-1 2000	Barley *AC Rosser*	Canada Brookdale, Manitoba	480SC	2	0.1310–0.2020	0.1152–0.1833	hay	14 14	3.445 2.933
							straw	43 43	0.603 0.606
200806 J6081-00H M-000715-01-1 2000	Barley *Bedford*	Canada ClanwilliamManitoba	480SC	2	0.1270–0.2040	0.1158–0.1826	hay	14	2.718
							straw	65 65	0.294 0.396
200806 J6082-00H M-000715-01-1 2000	Barley *AC Metcalf*	Canada Marcelin, Saskatchewan	480SC	2	0.1240–0.2010	0.0316–0.0508	hay	12 12	1.220 1.133
							straw	48 48	0.348 0.349
200806 J6083-00H M-000715-01-1 2000	Barley *Harrington*	Canada Rosthem, Saskatchewan	480SC	2	0.1270–0.2010	0.0315–0.0501	hay	12 12	2.534 2.246
							straw	43 43	0.774 0.751
200806 J6084-00H M-000715-01-1 2000	Barley *Harrington*	Canada Wakaw, Saskatchewan	480SC	2	0.1270–0.2000	0.1162–0.1838	hay	15 15	3.366 3.715
							straw	34 34	0.911 1.008
200806 J6085-00H M-000715-01-1 2001	Barley *Wheat*	Canada Lacombe, Alberta	480SC	2	0.1390–0.2110	0.1383–0.2110	hay	13 13	1.375 1.178
							straw	71 71	0.161 0.139

Report No Trial No. Doc No Year	Crop *Variety*	Country	Application				Residues		
			FL	No	kg/ha (ai)	kg/hL (ai)	Portion analysed	DALT (days)	Total residue prothioconazole (mg/kg)
200806 J6086-00H M-000715-01-1 2001	Barley *Wheat*	Canada Penhold, Alberta	480SC	2	0.1330–0.2120	0.1325–0.2109	hay	13 13	1.151 1.514
							straw	71 71	0.258 0.178
200806 J6087-00H M-000715-01-1 2000	Barley *Stein*	Canada Rosthem, Saskatchewan	480SC	2	0.1240–0.2052	0.1150–0.1832	hay	13 13	1.865 2.021
							straw	52 52	0.750 0.766
200806 J6088-00H M-000715-01-1 2000	Barley *AC Harper*	Canada Kipp, Alberta	480SC	2	0.1270–0.2090	0.0633–0.1016	hay	14 14	0.697 0.512
							straw	47 47	0.076 0.063
200806 J6089-00H M-000715-01-1 2000	Barley *Lacombe*	Canada Leduc, Alberta	480SC	2	0.1290–0.2090	0.1130–0.1833	hay	15 15	0.890 0.941
							straw	33 33	0.251 0.278
200806 J6090-00H M-000715-01-1 2000	Barley *Excel*	Canada Delisle, Saskatchewan	480SC	2	0.1270–0.2010	0.0320–0.0511	hay	15 15	1.747 1.843
							straw	30 30	1.056 1.003
200806 J6091-00H M-000715-01-1 2000	Barley *Chapais*	Canada St-Paul-d'Abbotsford, Quebec	480SC	2	0.1390–0.2090	0.281–0.465	hay	15 15	4.197 3.931
							straw	36 36	1.871 1.439

Rape forage

Table 76 Results of residue trials conducted on prothioconazole on oil rape in EU

Country Year	Crop Variety	FL	Application			Portion analysed	DALT [a] [days]	JAU 6476-desthio [mg/kg]	Report No. Trial No. Doc No
			No.	kg/ha ai	kg/hL ai				
Germany 2000	Rape seed	250 EC	2	0.175	0.0583	Green material	0[b] 0	< 0.05 0.75	RA-2088/00 R 2000 0079/0 M-091148-01-1
						Pod	41 56	< 0.05 < 0.05	
						Rest of plant	41 56	< 0.05 < 0.05	

Country Year	Crop Variety	FL	Application			Portion analysed	DALT [a] [days]	JAU 6476-desthio [mg/kg]	Report No. Trial No. Doc No
			No.	kg/ha ai	kg/hL ai				
Sweden 2000	Rape seed	250 EC	2	0.175	0.0583	Green material Pod Rest of plant	0[b] 0 42 56 42 56	0.21 0.85 < 0.05 < 0.05 < 0.05 0.05	RA-2088/00 R 2000 0419/2 M-091148-01-1
France 2000	Rape seed	250 EC	2	0.175	0.0583	Green material Pod Rest of plant Straw	0[b] 0 42 42 56	< 0.05 0.78 0.05 < 0.05 < 0.05	RA-2088/00 R 2000 0420/6 M-091148-01-1
Great Britain 2000	Rape seed	250 EC	2	0.190 0.175	0.0583	Green material Pod Rest of plant Straw	0[b] 0 42 42 56	< 0.05 0.54 < 0.05 < 0.05 0.07	RA-2088/00 R 2000 0421/4 M-091148-01-1
Germany 2001	Rape seed Express	250 EC	2	0.175	0.0583	Green material Straw	0 57	0.70 0.07	RA-2178/01 R 2001 0515/0 M-035525-01-1
Great Britain 2001	Rape seed Madrigal	250 EC	2	0.175 0.163	0.0583	Green material Straw	0 56	0.93 < 0.05 0.01	RA-2178/01 R 2001 0516/9 M-035525-01-1
France 2001	Rape seed Zenith	250 EC	2	0.175	0.0583	Green material Straw	0 59	0.80 0.05	RA-2178/00 R 2001 0517/7 M-035525-01-1
France 2001	Rape seed Capitol	250 EC	2	0.190 0.175	0.0583	Green material Straw	0 56	1.1 0.05	RA-2178/00 R 2001 0518/5 M-035525-01-1
France 2000	Rape seed Olara	250 EC	2	0.175	0.0583	Green material Pod Rest of plant Straw	0[b] 0 41 41 56	0.10 0.64 < 0.05 < 0.05 < 0.05	RA-2089/00 R 2000 0080/4 M-074984-01-1

Country Year	Crop Variety	FL	Application			Portion analysed	DALT [a] [days]	JAU 6476-desthio [mg/kg]	Report No. Trial No. Doc No
			No.	kg/ha ai	kg/hL ai				
France 2000	Rape seed Ebonite	250 EC	2	0.175	0.0583	Green material Pod Rest of plant Straw	0[b] 0 42 42 55	< 0.05 0.94 0.15 < 0.05 0.09	RA-2089/00 R 2000 0422/2 M-074984-01-1
France 2001	Rape seed Capitole	250 EC	2	0.175	0.0583	Green material Straw	0 56	0.85 0.08	RA-2179/01 R 2001 0519/3 M-033374-01-1
France 2001	Rape seed Constant	250 EC	2	0.175	0.0583	Green material Straw	0 56	0.97 0.20	RA-2179/01 R 2001 0520/7 M-033374-01-1

[a] Days after last treatment

[b] Prior to last treatment

Peanuts forage and hay

Table 77 Results of residue trials conducted with four applications of 480 SC formulation of prothioconazole on peanuts in the USA

Report No Trial No. Doc No Year	Crop *Variety*	Country	Application		Residues		
			kg/ha (ai)	kg/hL (ai)	Portion analysed	DALT (days)	total residue prothioconazole (mg/kg)
200508 J6029-00D M-001548-01-1 2000	Peanut *Georgia Greens*	USA Tifton, Georgia	0.202	0.137–0.148	Hay	7 7 14 14 21 21 28 28	2.359 2.420 4.350 2.908 3.385 3.958 2.066 3.781
200508 J6030-00H M-001548-01-1 2000	Peanut *VA 98R*	USA Suffolk, Virginia	0.203–0.208	0.0962–0.107	Hay	14 14	2.787 3.741
200508 J6031-00H M-001548-01-1 2000	Peanut *NC 12C, Lot G-2204*	USA Jamesville North Carolina	0.202–0.203	0.0702–0.0776	Hay	13 13	1.645 2.921
200508 J6032-00H M-001548-01-1 2000	Peanut *VA-C-92R, CV92R54399*	USA Roper, North Carolina	0.197–0.199	0.0707–0.0778	Hay	13 13	3.831 2.289

Report No Trial No. Doc No Year	Crop *Variety*	Country	Application		Residues		
			kg/ha (ai)	kg/hL (ai)	Portion analysed	DALT (days)	total residue prothioconazole (mg/kg)
200508 J6033-00H M-001548-01-1 2000	Peanut *Georgia Green*	USA Inaha, Georgia	0.197–0.203	0.148–0.161	Hay	15 15	0.989 1.249
200508 J6034-00H M-001548-01-1 2000	Peanut *AgraTech 201*	USA Herod, Georgia	0.201–0.204	0.158–0.165	Hay	14 14	2.740 2.036
200508 J6035-00H M-001548-01-1 2000	Peanut *Georgia Green*	USA Columbia, Alabama	0.201–0.203	0.154–0.171	Hay	15 15	3.044 2.574
200508 J6036-00H M-001548-01-1 2000	Peanut *VA 98R*	USA Knightdale, North Carolina	0.201–0.207	0.0601–0.0670	Hay	15 15	1.863 2.342
200508 J6037-00H M-001548-01-1 2000	Peanut *Georgia Green*	USA Vero Beach, Florida	0.202–0.204	0.133–0.141	Hay	14 14	2.235 1.709
200508 J6038-00H M-001548-01-1 2000	Peanut *TAMRun*	USA Vernon, Texas	0.201–0.206	0.0576–0.0645	Hay	14 14	4.458 2.801
200508 J6039-00H M-001548-01-1 2000	Peanut *TAMRun*	USA Vernon, Texas	0.201–0.203	0.0575–0.0643	Hay	14 14	2.564 3.025
200508 J6040-00H M-001548-01-1 2000	Peanut *Spanco*	USA Eakly, Oklahoma	0.202–0.211	0.154–0.161	Hay	15 15	1.797 2.799

Soya bean forage

Table 78 Total residues deriving from trials conducted with three applications of prothioconazole 480 SC on soya beans in the USA

Report No Trial No. Doc No Year	Crop Variety	Country	Application		Residues		
			kg/hL (ai)	GS	Portion analysed	DALT (days)	total residue prothioconazole (mg/kg)
RAJAY026	Soya	USA	0.097–	71	Forage	0	2.26

Report No Trial No. Doc No Year	Crop Variety	Country	Application		Residues		
			kg/hL (ai)	GS	Portion analysed	DALT (days)	total residue prothioconazole (mg/kg)
JA014-04D-P1 M-270206-01-1 2004	Pioneer 96M20	Molino, Florida	0.105			0 3 3 7 7 10 10 14 14	3.37 1.20 1.50 0.63 0.75 0.54 0.50 0.33 0.37
					hay	0 0 3 3 7 7 10 10 14 14	19.2 13.2 6.75 6.40 2.70 2.55 1.56 1.64 1.27 1.52
RAJAY026 JA019-04D-P1 M-270206-01-1 2004	Soya Stine 2788	USA Seymour, Illinois	0.118–0.121	67	forage	0 0 3 3 7 7 10 10 14 14	3.71 3.60 2.47 2.01 1.19 1.43 1.12 1.12 0.48 0.43
					hay	0 0 3 3 7 7 10 10 14 14	19.6 18.1 8.94 10.2 6.18 5.14 4.12 5.01 1.70 1.92
RAJAY026 JA015-04H-P1 M-270206-01-1 2004	Soya Pioneer RR 97B52	USA Tifton, Georgia	0.1006–0.1046	67	forage hay	7 7 7 7	1.39 1.09 5.63 2.35
RAJAY026 JA016-04H-P1 M-270206-01-1 2004	Soya Pioneer 9492RR	USA Leland, Mississipi	0.0951–0.1047	69	forage	7 7	1.99 1.61
					hay	7 7	5.90 6.89
RAJAY026 JA016-04H-P2 M-270206-01-1 2004	Soya Pioneer 9492RR	USA Leland, Mississipi	0.0972–0.1020	79	seed	20 20	< 0.05 0.055
					hay	7 7	6.74 6.04
RAJAY026 JA021-04H-P1 M-	Soya	USA Springfield	0.1115–0.1151	67	forage	5 5	1.34 1.51

Report No Trial No. Doc No Year	Crop Variety	Country	Application		Residues		
			kg/hL (ai)	GS	Portion analysed	DALT (days)	total residue prothioconazole (mg/kg)
270206-01-1 2004	NKS28W2	Nebraska			hay	5 5	4.78 5.01
RAJAY026 JA022-04H M-270206-01-1 2004	Soya Jim	USA Sabin, Minnesota	0.1354–0.149	73	forage	7 7	0.705 0.736
					hay	7 7	4.14 4.29
RAJAY026 JA024-04H-P1 M-270206-01-1 2004	Soya Croplan RT0907	USA Britton, South Dakota	0.158–0.159	62	forage	7 7	2.17 1.70
					hay	7 7	7.16 5.47
RAJAY026 JA025-04H-P1 M-270206-01-1 2004	Soya Croplan RT1447	USA Dumfries, Minnesota	0.0851–0.0863	63	forage	7 7	1.82 1.56
					hay	7 7	6.65 8.23
RAJAY026 JA026-04HA M-270206-01-1 2004	Soya SC9374	USA New Holland, Ohio	0.1044–0.1045	69	forage	6 6	1.03 1.19
					hay	6 6	1.62 1.46
RAJAY026 JA027-04H-P1 M-270206-01-1 2004	Soya 92M70	USA Bagley, Iowa	0.0911–0.0959	67	forage	7 7	1.61 1.51
					hay	7 7	6.93 5.69
RAJAY026 JA028-04H-P1 M-270206-01-1 2004	Soya DynaGro DG 32M32RR	USA York, Nebraska	0.0799–0.0826	18	forage	7 7	0.967 0.656
					hay	7 7	4.31 4.32
RAJAY026 JA030-04H-P1 M-270206-01-1 2004	Soya Pioneer 93M80	USA Richland, Iowa	0.0928–0.1126	75	forage	7 7	0.485 0.091
					hay	7 7	6.99 4.28
RAJAY026 JA031-04H-P1 M-270206-01-1 2004	Soya Pioneer 91M50	USA Geneva, Minnesota	0.1003–0.1028	64	forage	7 7	2.31 2.75
					hay	7 7	8.35 8.11
RAJAY026 JA032-04H-P1 M-270206-01-1 2004	Soya Pioneer 93B85	USA Hudson, Kansas	0.0883–0.0895	77	forage	6 6	1.19 1.34
					hay	6 6	5.25 5.26
RAJAY026 JA018-04HA M-270206-01-1 2005	Soya AG4403RR	USA Proctor, Arkansas	0.1056–0.1075	65	forage	7 7	4.45 4.04
					hay	7 7	17.6 18.9
RAJAY026 JA020-04HA M-270206-01-1 2005	Soya Taylor427RR	USA Stilwell, Kansas	0.1083–0.1116	75	forage	7 7	1.61 1.57
					hay	7 7	7.21 5.17

Report No Trial No. Doc No Year	Crop Variety	Country	Application		Residues		
			kg/hL (ai)	GS	Portion analysed	DALT (days)	total residue prothioconazole (mg/kg)
RAJAY026 JA029-04HA M-270206-01-1 2005	Soya Dairyland 3410 RR	USA Sheridan, Indiana	0.07580–0.08616	69	forage	7 7	< 0.05 < 0.05
					hay	6 6	6.93 4.26
RAJAY026 JA033-04HA M-270206-01-1 2005	Soya NK43-B1	USA Carlyle, Illinois	0.08639–0.1104	66	forage	7 7	0.091 0.088
					hay	7 7	2.38 1.91

Fate of residues during storage and processing

In processing

A hydrolysis study under conditions representative for core processing procedures was conducted in order to determine their possible influence on the nature of the residues (Gilges, M. (2001). [PhenyI-UL-^{14}C] prothioconazole was dissolved at concentrations of approximately 4.6 mg/L in citrate buffers in drinking water which were incubated at 90 °C at pH 4 for 20 minutes (pasteurisation), l00 °C at pH 5 for 60 minutes (baking, brewing and boiling) and l20 °C at pH 6 for 20 minutes (sterilisation). After incubation the samples were analysed by liquid scintillation counting and HPLC to establish recoveries of radioactivity and determination of residue components.

The results obtained under the different processing conditions are presented in Table 79.

Table 79 Summarised Results of Hydrolytic Degradation of prothioconazole (% of applied radioactivity)

Incubation conditions	Recovery (%)	prothioconazole	JAU 6476-desthio (M04)	Sum of Minor Degradation Products
pH 4, 90 °C	97.7	89.1	2.8	5.7
pH 4, control		94.3	1.2	4.5
pH 5, 100 °C	96.7	86.2	7.4	3.1
pH 5, control		93.0	1.5	5.5
pH 6, 120 °C	94.4	79.0	10.6	4.8
pH 6, control		90.9	3.4	5.7

Uses

The use of prothioconazole in North America is intended for use in cereals, rape, peanut, dried beans/peas and sugar beet. Processing studies were conducted on wheat, rape seed and peanuts.

Wheat grain, bran, flour, germ

A field trial was conducted in Stilwell, Kansas, USA to measure the magnitude of prothioconazole residues in wheat grain, aspirated grain fractions, bran, flour, germ, middling and shorts following two foliar spray applications of prothioconazole 480 SC to wheat (Kraai, MJ, 2004). The total amount of prothioconazole 480 SC applied to the wheat represented a five-fold (5×) exaggeration of the maximum recommended label use rate.

Mature wheat grain was harvested from the treated plot at BBCH growth stage 89 (fully ripe), which was 47 days after the last treatment. A single composite sample of wheat grain was collected at the earliest commercial harvest from both the treated plot and the control plot. Sub-samples of the

wheat grain were removed for analysis. The remainder of the wheat grain was used to produce aspirated grain fractions and then processed into bran, flour, germ, middling, and shorts. Processing was performed using procedures which simulated commercial processing practices.

The residues of prothioconazole and JAU6476-desthio were measured as JAU6476-desthio and JAU6476 sulfonic acid and quantified by HPLC/triple stage quadrupole mass spectrometry. In the method, residues of prothioconazole are converted to JAU6476 sulfonic acid and/or JAU6476-desthio, while residues of JAU6476-desthio remain unchanged. The individual residues were summed to give a total prothioconazole derived residue. The LOQ for total prothioconazole-derived residue was 0.02 mg/kg for wheat grain, bran, flour, germ, middling and shorts. The LOQ for total prothioconazole derived residue was 0.25 mg/kg for aspirated grain fractions.

The results are summarised in Table 80.

Table 80 Results from processing studies with two applications of prothioconazole 480 SC on wheat

Report No Trial No. Doc No Year	Crop Variety	Country	Application		Residues			Transfer factors [b]
			kg/ha (ai)	kg/hL (ai)	Portion analysed	DALT (days)	Total residue prothioconazole (mg/kg)	
200521 J6065-00P M-000665-01-1 2000	Wheat, winter Wheat Karl 92	USA Stilwell, Kansas America, North	0.632–1.01	0.662–1.06	grain asp grain [a] bran flour germs middling shorts	47 47 47 47 47 47 47	0.05 12.5 0.12 < 0.02 0.10 0.03 0.05	– 250 2.4 < 0.4 2 0.6 1

[a] aspirated grain fraction

[b] Processing Factor = Average residue in processed sample / residue in unprocessed sample.

Canola seed, canola meal and canola refined oil

A field trial was conducted in Sheffield, Ontario to measure the magnitude of prothioconazole residues in canola seed, canola meal and canola refined oil following two foliar spray applications of prothioconazole 480 SC with 1.0 kg ai/ha, which corresponded to a five-fold (5×) exaggeration of the maximum recommended label use rate.

Mature canola plants were cut at a 47-day pre-harvest interval (PHI) from the control and treated plots and allowed to dry in the field. Five days after the cutting, a single composite sample of mature seed (BBCH growth stage 89; fully ripe) was mechanically collected from both the treated plot and the control plot. Sub-samples of the canola seed were removed for analysis. The remainder of the seed was processed into meal and refined oil (bleached and deodorized). Processing was performed using procedures which simulated commercial processing practices.

The residues of prothioconazole and JAU6476-desthio were measured as JAU6476-desthio and JAU6476 sulfonic acid and quantified by HPLC/triple stage quadrupole mass spectrometry. In the method, residues of prothioconazole are converted to JAU6476 sulfonic acid and/or JAU6476-desthio, while residues of JAU6476-desthio remain unchanged. The individual residues were summed to give a total prothioconazole derived residue. The LOQ for total prothioconazole derived residue was 0.02 mg/kg for canola seed, meal and refined oil. The results are summarised in Table 81.

Table 81 Results of processing canola seed treated with exaggerated dose rate of prothioconazole

Report No Trial No. Doc No Year	Crop Variety	Country	Application		Residues			Mean transfer factors [a]
			kg/ha (ai)	kg/hL (ai)	Portion analysed	DALT (days)	Total residue prothioconazole (mg/kg)	
200953 J619CN02 M-060246-01-1 2000	Rape Invigor 2473	Canada Sheffield Ontario	1.022–1.030	0.4892–0.5081	seed meal oil, refined	47 47 47	0.03 < 0.02 < 0.02	< 0.7 < 0.7

[a] Processing Factor = Average residue in processed sample / residue in unprocessed sample.

A field trial was conducted in Tifton, Georgia, USA to measure the magnitude of prothioconazole residues in peanut nutmeats, peanut meal, peanut refined oil, dry roasted peanuts and peanut butter following four foliar spray applications of prothioconazole 480 SC to peanut plants (Lenz, C.A.; 2004). The applications were performed at a target rate of 1.0 kg ai/ha with a 14 (±2 day) interval between applications and the last application being made at 14 days prior to digging mature peanuts. The total amount of prothioconazole 480 SC applied to the peanut plants represented a five-fold (5×) exaggeration of the maximum recommended label use rate. Processing was performed using procedures which simulated commercial processing practices.

The residues of prothioconazole and JAU6476-desthio were measured as JAU6476-desthio and JAU6476 sulphonic acid and quantitated by HPLC/triple stage quadrupole mass spectrometry using stable-labelled internal standards according to method RPA JA/03/01. The LOQ for total prothioconazole derived residue was 0.02 mg/kg for peanut nutmeats, peanut meal, peanut refined oil, dry roasted peanuts and peanut butter. Recovery of prothioconazole and JAU6476-desthio from peanut nutmeat fortified at 0.02 ppm ranged from 81% to 87% and from 90% to 97%, respectively. Recovery of prothioconazole and JAU6476-desthio from peanut nutmeat fortified at 0.10 ppm ranged from 83% to 89% and from 90% to 92%, respectively.

Recovery of prothioconazole and JAU6476-desthio from peanut meal fortified at 0.30 ppm for high level method validation ranged from 82% to 84% and from 98% to 99%, respectively.

The results are shown in Table 82.

Table 82 Results from processing studies on peanuts

Report No Trial No. Doc No Year	Crop Variety	Country	Application				Residues			Mean transfer factors*
			FL	No	kg/ha (ai)	kg/hL (ai)	Portion analysed	DALT (days)	Total residue (mg/kg)	
200518 J619PE02 J6041-00P GLP no 2000	Peanut Georgia Greens	USA Tifton, Georgia America, North	480 SC	4	1.01-1.01	0.686-0.738	meat meal oil, refined peanut, roasted peanut butter	14 14 14 14 14	2.43 4.54 <0.01 1.30 1.42	 1.8 <0.1 0.5 0.6

*Transfer Factor = Average residue in processed sample / residue in unprocessed sample.

A field trial was conducted in Leland, MS, USA to measure the magnitude of prothioconazole residues in soya bean aspirated grain fractions and soybean processed commodities of meal, hulls and refined oil following three foliar spray applications of prothioconazole 480 SC to soya bean plants (Duah, F.K. and Harbin, A. M.; 2006). The total amount of prothioconazole 480 SC applied to the

soya bean plants represented a five-fold (5×) exaggeration of the maximum recommended label use rate. Samples were collected 22 days after last application.

The seed sample was further processed into food or feed fractions. Processing was performed using procedures which simulated commercial processing practices.

The total prothioconazole residue was determined with LC-MS/MS method as for peanut. The LOQ was 0.05 mg/kg for soya bean seed, meal, hulls and refined oil and 1.0 mg/kg for soya bean aspirated grain fractions. The recoveries ranged from 73 to102% between 0.05–0.2 mg/kg spike levels.

The results are summarised in Table 83.

Table 83 Results from processing studies on soya beans

Report No Trial No. Doc No Year	Crop Variety	Country	Application				Residues			Mean transfer factors **
			FL	No	kg/ha (ai)	kg/hL (ai)	Portion analysed	DALT (days)	Total residue JAU 6476 (mg/kg)	
RAJAY027 JA035-04P M-270263-01-1 2004	Soya Pioneer 9492RR	USA Leland, Mississippi	480 SC	3	0.731-0.753	0.459-0.479	Seed Asp. Grain* Meal Hull Oil refined	22 22 22 22 22	0.31 23.20 0.06 0.17 <0.05	 75 0.2 0.5 <0.2

* Aspirated grain fractions

** Transfer factor = Average residue in processed sample / residue in unprocessed sample.

RESIDUES IN ANIMAL COMMODITIES

Farm animal feeding studies

Cattle

The cattle feeding studies were conducted with the parent compound prothioconazole and JAU 6476-desthio, which is the predominant metabolite in plant materials.

Ten lactating German dairy cattle (breed: Holstein Friesian; three cows/dose group and one control cow) were dosed orally (Heinemann, O, Auer, S, 2001), via capsule, for 28 consecutive days with JAU6 476-desthio at dose rates of either 0 mg/kg feed (control), 4 mg/kg feed, 25 mg/kg feed or 100 mg/kg feed. These feeding levels were chosen to cover the dietary burden for both, the US and EU. The actual average dose rates were 1.3×, 7.3× and 31× the anticipated maximum dietary burden.

Milk was collected for analysis twice daily and three times weekly during the dosing period and composited for each cow. In addition, a portion of the morning milk from one cow of the highest dose level, 31×, was subjected to an accumulation test in milk fat on the day before sacrifice. At the end of the 28-day dosing period, the cows were sacrificed within 24 hours after the last capsule treatment. The liver, kidney, fat (composite omental and peri-renal) and muscle (composite of loin, elbow and flank) were collected and weighed. Blood was washed off from the tissues. The tissue samples were weighed and stored at approximately 4 °C until they were individually chopped into small pieces and immediately transferred to a freezer (≤ –18°C). After freezing, the individual liver, kidney, muscle and fat samples were homogenised using dry ice and returned to the freezer for storage.

Tissue and milk samples from each animal were individually processed and analysed for JAU 6476-3-hydroxy-desthio (M14), JAU 6476-4-hydroxy-desthio (M15), and JAU 6476-desthio (M04) residues using the procedures described in the residue analytical method 00655

(Heinemann, 2001b) and its modification for milk M001 (Heinemann, 2001c) by HPLC/MS/MS. The LOQ were 0.01 mg/kg for muscle, liver, kidney and fat and 0.004 mg/kg for milk.

The stability of all analytes in tissues and milk was confirmed for a frozen storage interval of four weeks (kidney: three weeks). All tissue sample analyses in this study were completed within this storage interval.

During the analyses the recoveries of the analytes were tested with spiking control materials. The results are shown in Table 84.

Table 84 Concurrent recoveries of prothioconazole residues in muscle, liver, kidney and milk of cattle.

Sample material	Spike level mg/kg	M14	M15	JAU6476-desthio
Liver	0.01	90	90	96
	0.1	98	93	95
Kidney	0.01	98	98	98
	0.1	98	93	91
Muscle	0.01	95	95	100
	0.1	98	98	98
Fat	0.01	92	93	83
	0.1	94	95	83
Milk	0.004–0.1	89–104	83–102	86–103

The measured average concentrations for the individual constituents of the total residue are compiled in Table 85. The maximum residue observed in individual cattle is plotted against the administered doses. A good linear correlation is shown in Figure 4.

Table 85 Average residue concentrations (mg/kg) in the edible tissues of dairy cattle after 28 days of dosing with JAU 6476-desthio

Dose group	M14[a]	M15[a]	M04[a]	Total [b]	M14[a]	M15[a]	M04[a]	Total[b]
mg/kg feed	Liver				Kidney			
4	0.01	0.01	0.02	0.04	0.01	0.01	< 0.01	0.02
25	0.05	0.03	0.15	0.22	0.06	0.06	0.03	0.14
100	0.18	0.11	0.93	0.95	0.28	0.25	0.13	0.65
	Muscle				Fat			
4	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
25	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	0.01
100	< 0.01	< 0.01	< 0.01	0.02	0.01	0.01	0.05	0.07

[a] M14: JAU 6476-3-hydroxy-desthio, M15: JAU 6476-4-hydroxy-desthio, M04: JAU 6476-desthio

[b] Sum of M14, M15, and M04, expressed as mg/kg JAU 6476-desthio equivalents

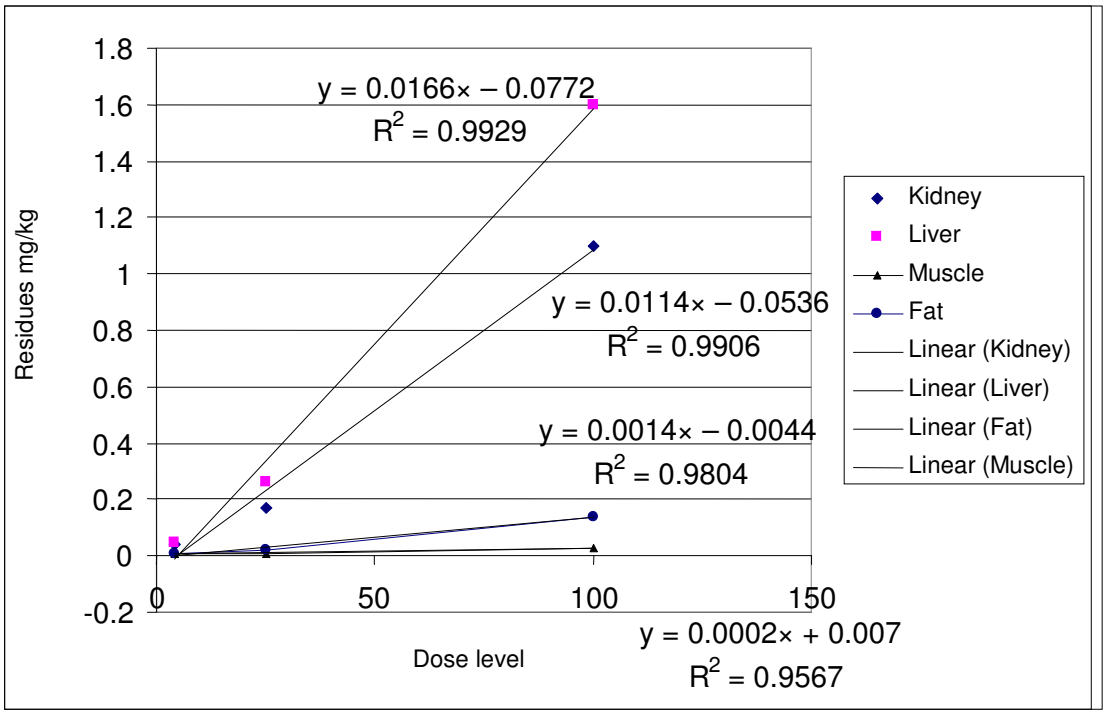


Figure 4 Maximum residues in cattle tissues observed at different dose levels

Milk

JAU6476-desthio total residues in milk at the 1.3× and 7.3× feeding levels were below the LOQ (0.004 mg/kg), whereas at the 31× feeding level, total residues increased from < 0.004 mg/kg (day 1) to a plateau level (day 4 to day 29) of 0.006 to 0.010 mg/kg for two animals and of 0.013 to 0.021 mg/kg for one animal. The time course of the total residues in the milk of the single animals is shown in Figure 4. Liquid-liquid partitioning of whole milk against n-hexane showed that M04 was in milk fat and the metabolites M14 and M15 remained in the aqueous phase. However, the total residues remained preferentially in the aqueous phase, i.e., 0.015 mg/kg with only 0.004 mg/kg in the n-hexane phase, indicating no accumulation in milk fat.

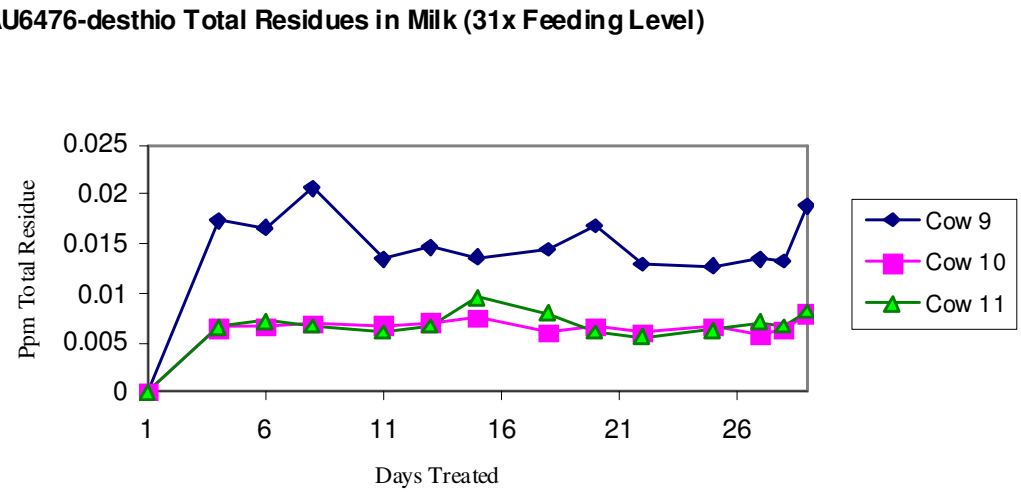


Figure 5 The sum of residues measured in milk of the highest dose group (31×) during the course of the dairy cattle feeding study.

Remark: Day 29 Morning milk.

In the control animal tissues and milk, no residues were found above the respective LOQ levels.

In a second study (Duah, FK, 2004) ten lactating dairy cows (Bos Taurus three in each treatment group and one control cow) were dosed orally, via capsule, for 29 consecutive days with prothioconazole at dose rates corresponding to 0 mg/kg feed (control animal dosed with only empty gelatine capsules), 9.9 mg/kg feed, 29.5 mg/kg feed, and 98.4 mg/kg feed.

Milk was collected twice daily during the dosing period. Milk samples from the 29.5 and 98.4 mg/kg dose groups were analysed for study days 0, 4, 8, 12, 16, 18, 20, 22, 24, 26 and 28. Additionally, a portion of the day 26 milk sample from the highest dose group was separated into cream and skim milk, and each was analysed. On study day 29, the animals were sacrificed and composite fat, kidney, liver, and composite muscle samples were collected for analysis. The samples were analysed for prothioconazole residues (prothioconazole, JAU6476desthio and JAU6476-4-hydroxy) by LC-MS/MS using stable-labelled internal standards according to US method (report No 200537). The LOQ was 0.005 mg/kg in milk, 0.01 mg/kg in skim milk, milk cream, liver, kidney and muscle, and 0.05 mg/kg in fat.

The concurrent mean recoveries were above 80% with a maximum of 16.5% standard deviation.

In general, the prothioconazole residues in milk reached a plateau within the first week of dosing. The total prothioconazole residues in kidney and liver were proportional to the doses received. Prothioconazole residues were generally the highest in liver and kidney and lowest in milk and muscle. The total prothioconazole residue in fat, milk and muscle from all dose groups were too low to allow any estimation of proportionality between doses and residue levels.

The highest total prothioconazole residue in the milk from the 5.0× dose group was equal to or less than 0.006 mg/kg. All milk samples from the 1.5× dose group contained < 0.005 mg/kg (< LOQ) total prothioconazole residue. Minimal concentration (1.1× concentration) of JAU6476 residues occurred in cream and no concentration (< 1× concentration) occurred in skim milk.

The milk from the 1.5× and 5.0× dose groups and the cream and skim milk from the 26-day milk were analysed. Generally, the total prothioconazole residues reached a plateau within approximately the first week of dosing. The total prothioconazole residue (residue of prothioconazole,

JAU6476-desthio and JAU6476-4-hydroxy combined) in the milk from the 5.0× dose group ranged from < 0.005 mg/kg to 0.006 mg/kg. The milk from the 1.5× dose group contained < 0.005 mg/kg total prothioconazole residue. The measured total prothioconazole residue in the 26-day milk and cream were 0.004 mg/kg and 0.0044 mg/kg, respectively. Therefore, there was no evidence of significant concentration of prothioconazole residues into milk cream. The total prothioconazole residue did not concentrate in skim milk.

A summary of the prothioconazole residues found in the tissues is given in Table 86.

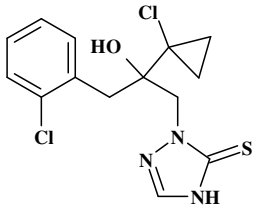
Table 86 Average residue concentrations (mg/kg) in the edible tissues of dairy cattle after 29 days of dosing with prothioconazole

Dose group mg/kg feed	prothioconazole	JAU6476-Desthio	JAU6476-4 Hydro-xy	Total prothioconazole [a]	prothioconazole	JAU6476-Desthio	JAU6476-4 Hydro-xy	Total prothioconazole [a]
	Fat				Kidney			
9.9	< 0.012	< 0.005	< 0.008	< 0.05	0.053	0.003	0.015	0.07
29.5	0.014	< 0.005	< 0.008	< 0.05	0.148	0.005	0.054	0.21
98.4	0.029	0.006	0.013	< 0.05	0.551	0.011	0.234	0.80
	Liver				Muscle			
9.9	0.047	0.005	0.047	0.10	–	–	–	–
29.5	0.107	0.010	0.162	0.28	0.002	0.001	0.001	< 0.01
98.4	0.339	0.023	0.433	0.80	0.006	0.001	0.002	0.01

[a] Sum of individual prothioconazole, JAU6476-desthio and JAU6476-4-hydroxy residues (in mg/kg parent equivalent)

APPRAISAL

Prothioconazole was considered for the first time by the present meeting. It is a systemic fungicide with a triazolinthione structure. The manufacturing process is not enantiomer-selective. All technical quality prothioconazole is produced as a 50:50 racemate.



IUPAC: 2-[(2*RS*)-2-(1-chlorocyclopropyl)-3-(2-chlorophenyl)-2-hydroxypropyl]-2H-1,2,4-triazole-3(4H)-thione

CAS: 2-[2-(1-chlorocyclopropyl)-3-(2-chlorophenyl)-2-hydroxypropyl]-1,2-dihydro-3*H*-1,2,4-triazole-3-thione.

The code and descriptive names of metabolites mentioned in the appraisal are:

M01 JAU 6476-S-methyl

M02 JAU 6476-sulfonic acid

M03 JAU 6476-triazolinone

M04 JAU 6476-desthio

M05 JAU 6476-N-glucuronide

M06 JAU 6476-S-glucuronide

M08	JAU 6476-4-hydroxy
M09	JAU 6476-benzylpropyldiol
M11	JAU 6476-disulfide
M12	JAU 6476-thiazocine
M13	1,2,4-triazole
M14	JAU 6476-desthio-3-hydroxy
M15	JAU 6476-desthio-4-hydroxy
M16	JAU 6476-desthio-5-hydroxy
M17	JAU 6476-desthio-6-hydroxy
M18	JAU 6476-desthio-α-hydroxy
M19	JAU 6476-desthio-α-acetoxy
M20	2-chlorobenzoic acid
M21	JAU 6476-desthio-3-hydroxy-glucoside
M22	JAU6476-desthio-4-hydroxy-glucoside
M23	JAU 6476-desthio-6-hydroxy-glucoside
M24	JAU 6476-desthio-hydroxy-dienyl-cysteine
M28	JAU 6476-desthio-hydroxy-methoxy
M29	Triazolylacetic acid (TAA)
M30	Triazolylhydroxypropionic acid (THP)
M31	Triazolylalanine (TA)
M32	JAU 6476-desthio-3,4-dihydroxy-diene
M33	JAU 6476-desthio-3,4-dihydroxy
M34	JAU 6476-desthio-dihydroxy
M36	JAU 6476-desthio-4,5-dihydroxy-diene
M38	JAU 6476-desthio-dihydroxy-diene
M40	JAU 6476-dihydroxy-diene
M44	JAU 6476-desthio-phenyl-cysteine
M45	JAU 6476-triazolyl-ethanol
M46	JAU 6476-triazolyl-ethanol-glucoside
M52	JAU 6476-desthio-3,4-dihydroxy-dienyl-glucuronide
M54	JAU 6476-desthio–3-hydroxy-glucoside-malonic acid
M55	JAU 6476-desthio-4-hydroxy-glucoside-malonic acid
M56	JAU 6476-desthio-6-hydroxy-glucoside-malonic acid
M59	JAU 6476-hydroxy-sulfonic acid glucoside
M60	JAU 6476-hydroxy-disulfonic acid glucoside
M62	JAU 6476-triazolyl-sulfonic acid-ethanol-glucoside
M71	JAU 6476-desthio-glucuronide
M73	JAU 6476-desthio-dihydroxy-dienyl-glucuronide
M74	JAU 6476-desthio-4-hydroxy-glucuronide
M75	JAU 6476-desthio-hydroxy-glucuronide
M80	Thiocyanate
M82	JAU 6476-desthio-hydroxy-methoxy-sulfate
M84	JAU 6476-desthio-hydroxy-sulfate
M85	JAU 6476-desthio-4,5-dihydroxy-dienyl-glucuronide
M87	JAU 6476-desthio-3-hydroxy-glucuronide

The Meeting received comprehensive information for the evaluation of prothioconazole as a new compound in accordance with the data requirements specified in the *FAO Manual*[8].

The metabolism of prothioconazole, in plants and animals was investigated using [phenyl-UL-^{14}C]prothioconazole referred to as phenyl-label, and [3,5-triazole-^{14}C] labelled parent compound referred to as triazole-label. In addition, studies were conducted using [phenyl-UL-^{14}C]- and [3,5-triazole-^{14}C] labelled prothioconazole-desthio *(M04)* which is derived from the parent compound by losing the thione group.

Animal metabolism

Information was provided on the metabolism of prothioconazole in rats, lactating goats and laying hens.

When rats were orally dosed the prothioconazole was rapidly absorbed and excreted mainly via the bile. The major types of metabolic reactions identified were conjugation with glucuronic acid, oxidative hydroxylation of the phenyl moiety and desulfuration. Many of the metabolites were derived from prothioconazole-desthio.

Prothioconazole-S-glucuronide, prothioconazole-desthio and prothioconazole were the principal components, in addition to 10 minor metabolites identified in excreta. The studies with prothioconazole showed that metabolite prothioconazole-desthio, which is the major metabolite of prothioconazole in wheat, amounted to about 18% of the administered dose occurred in the faeces, and a maximum 0.07% in the urine. A study with the metabolite prothioconazole-desthio, which is the major metabolite of prothioconazole in wheat, revealed that about 68% to 74% of the administered dose occurred in the faeces, and a maximum of 10% to 11% in the urine.

The goat metabolism studies followed the same design. In each trial one goat received 10 mg/kg body weight/day dose on three consecutive days in intervals of 24 h. The dose level corresponded to about 195 ppm test substance in the feed. The animals were sacrificed 5 h after administration of the final dose.

Following the administration of phenyl-, triazole-labelled prothioconazole or phenyl labelled prothioconazole-desthio, the goats excreted about 67, 59 and 74%% administered dose, respectively, within five hours after the last dose. About 0.02–0.05% of the total dose was found in the milk, and about 0.7–1.9% of the total dose was in the organs and tissues.

The TRR values, derived from the administration of labelled parent compound, expressed in mg as equivalents/kg sample material, were 6.1–6.2 mg/kg in liver, 4.5–6.8 mg/kg in kidney, 0.17–0.21 mg/kg in omental fat, 0.11–0.162 mg/kg perirenal fat, 0.11–0.15 mg/kg in subcutaneous fat and 0.08–0.14 mg/kg in muscle.

The metabolic profiles for milk and the edible tissues and organs showed that parent prothioconazole was a major compound in all tissues and organs (> 10% of TRR), but only of minor importance in milk (< 1–3% of TRR or ≤ 0.005 mg/kg). Other metabolites detected in all matrices were prothioconazole-S-glucuronide, prothioconazole–desthio and a number of the hydroxy moiety containing metabolites *(M08, M15, M32, M38, M40,)*, their glucuronides *(M10, M49, M52, M69, M72, M73, M74)* and sulfate conjugates *(M82, M83, M84)*. Following the administration of triazole labelled prothioconazole the only label specific metabolite identified was thiocyanate: 41.1% of TRR, 0.061 mg/kg in milk, 30% in muscle, 12% in fat, 9% in kidney and 2% in liver. Thiocyanate is well known as the main detoxification product after cyanide exposure, and it is a natural constituent of milk.

[8] FAO. 2002. Submission and evaluation of pesticide residues data for the estimation of maximum residue levels in food and feed. Appendix IX. Maximum proportion of agricultural commodities in animal feed. *FAO Plant Production and Protection Paper*, 170.

The administration of phenyl-labelled prothioconazole-desthio resulted in somewhat higher level of total residues. The presence of triazole derivatives or free 1,2,4-triazole at concentrations above 0.01 mg/kg was excluded in each matrix under investigation.

In order to simplify the metabolic pattern, the organs and milk of goat was subjected to acid hydrolysis. The large number of metabolites present in the extracts (M32, M36, M52, M71, M73, M74, M75, M84, M85, *M86 M87, M91*) was reduced to prothioconazole-desthio, *M14*, *M15*, *M33*, *M35* and *M71*.

When prothioconazole-desthio was administered to goat the proportion of identified/characterized metabolites in the TRR after the acid hydrolysis was higher in milk, muscle and kidney than without hydrolysis, and it was practically equal in liver (58.4% and 59.9%) and fat (75% and 74%)

Six laying hens were orally dosed with phenyl or triazole radiolabelled prothioconazole at a dose level of 10 mg/kg body weight. The hens received the doses on three consecutive days at intervals of 24 h. The animals were sacrificed 5 h after the administration of the final dose.

The edible tissues and organs (liver, fat and muscle), pooled excreta and eggs collected daily were analysed by HPLC and TLC. Extractability was high for all tissues and ranged from 77% to 98% of the TRR. The identification rates ranged from 42% and 84%.

About 78% of the phenyl labelled prothioconazole dose administered was already excreted five hours after the last dose. Very low amounts of the total dose were found in eggs during the experimental phase (about 0.01%) and in organs/tissues investigated after sacrifice of the animals (about 0.9%). In the study with the triazole label about 66% of the administered dose was excreted five hours after the last dose. Also very low amounts of the total dose were found in eggs during the experimental phase (about 0.01%) and in organs/tissues investigated after sacrifice of the animals (about 0.8%).

The TRR values, derived from the phenyl- and triazole labelled prothioconazole and expressed in mg as equivalents/kg sample material were, respectively, 4.0–3.5 mg/kg in liver, 0.036–0.05 mg/kg in eggs, 0.45–0.29 mg/kg in subcutaneous fat, 0.089–0.12 mg/kg in muscle.

The parent compound was the major residue component in liver (31% of TRR, 1.1 mg/kg), fat (30% of TRR, 0.14 mg/kg) and muscle (11% of TRR, 0.01 mg/kg). Metabolites exceeding 10% of TRR were prothioconazole-desthio (29.0% of TRR, 0.13 mg/kg) and prothioconazole -S-methyl (20% of TRR, 0.088 mg/kg) in fat, and prothioconazole-S-glucuronide in muscle (15.5% of TRR, 0.014 mg/kg), and liver (*M06*, 15% of TRR, 0.53 mg/kg). The other metabolites occurring in smaller proportion were *M05 M08*, *M10*, *M15, M80* and the label specific metabolites (*M45* and 1,2,4-triazole). All other metabolites identified were either glucuronic acid conjugates derived directly from prothioconazole or from the hydroxylated parent compound or sulfate and glucuronic acid conjugates *(M52, M82, M83, M84)* (in sum 14% of TRR, 0.47 mg/kg).

In eggs the major residue components were prothioconazole-S-glucuronide (24% of TRR, 0.012 mg/kg), prothioconazole-desthio (20% of TRR, 0.007 mg/kg), *M45* (15.6% of TRR, 0.008 mg/kg), 1,2,4-triazole (11% of TRR, 0.006 mg/kg), and thiocyanate (9.8% of TRR, 0.005 mg/kg). Prothioconazole (*3.6% of TRR, 0.002 mg/kg)*, *M15* and *M01* were also detected raging from 1.9% to 3.3% of the TRR.

In summary, the metabolic profile was similar in goats and hens and their edible tissues investigated in the studies with phenyl- and triazole-labelled prothioconazole. The parent compound was one of the major residues in most matrices of goat and hen with the exception of egg in which prothioconazole-desthio was predominant.

The majority of metabolites were derived from the intact parent molecule, retaining the triazolinthione structure, which was detected in all studies with prothioconazole, independent of the radiolabel used. A label specific metabolite common for hen and goat was thiocyanate. This metabolite was detected in all sample materials under investigation. It was a major metabolite in milk and muscle of goat and was detected at about 10% of the TRR in eggs of hens. Two additional label

specific metabolites were identified exclusively in laying hen: free 1,2,4-triazole and prothioconazole-triazolyl-ethanol, which were detected in all matrices, including eggs, but they were not present in milk, organs or edible tissues of goat.

The key metabolite in all matrices was prothioconazole-S-glucuronide. Due to the conjugation with glucuronic acid, the sulfur was protected against cleavage. Thus, the metabolic route via prothioconazole-desthio was impeded. Prothioconazole-desthio and all its derivatives accounted in each sample matrix, except in fat and eggs, for less than 20% of the TRR. The major metabolic routes include molecules containing the intact parent compound.

Plant metabolism

The behaviour and metabolism of prothioconazole after spray application in wheat, peanut and sugar beets was investigated using phenyl- and triazole-labelled parent compound. Additionally, the metabolism of phenyl-labelled prothioconazole after seed treatment of wheat and the metabolism of prothioconazole-desthio following spray application were studied.

When phenyl- and triazole-labelled prothioconazole was used for foliar treatment of wheat approximately at the recommended rate (0.2 kg/ha), the total radioactive residue (TRR) levels in forage, hay, straw and grain were 10 and 8.0 mg/kg, 8.9 and 11 mg/kg, 27 and 8 mg/kg and 0.08 and 5 mg/kg (ai equivalents), respectively.

When the seeds were treated at 1× rate the total radioactive residue (TRR) levels were very low and amounted to 0.02 mg/kg in forage, 0.02 mg/kg in hay, 0.03 mg/kg in straw and 0.008 mg/kg (as equivalents) in grain, respectively. Following the 5× treatment the TRR were 0.07 mg/kg in forage, 0.09 mg/kg in hay, 0.28 mg/kg in straw and < 0.01 mg/kg in grain.

Following foliar application with phenyl and triazole labelled parent compounds, the identified metabolites accounted respectively for 73% and 66% of the TRR in forage, 65% and 75% of the TRR in hay, 66% and 61% of the TRR in straw and 34% and 94% of the TRR in grain.

Prothioconazole was extensively metabolized in wheat. Prothioconazole-desthio was found as the main metabolite in all crop parts: forage, (35.4% of the TRR, 3.7 mg/kg), hay (18.5% of the TRR, 1.64 mg/kg), straw (22% of the TRR, 6.0 mg/kg) and grain (16% of the TRR, 0.014 mg/kg).

The hydroxylated metabolites of prothioconazole-desthio *(M14, M15, M17)* and the corresponding glucosides were present in forage, hay and straw, but wheat grain contained only M14, M15.

In addition, the parent compound and the following metabolites were identified in wheat forage, hay and straw: *M02*, *M03*, *M11* and *M18*.

Following the foliar application of prothioconazole-desthio, TRR in forage was 10 mg/kg (day 0) and 11 mg/kg (day 14). The TRRs in straw, and grain were 29 mg/kg and 2.9 mg/kg, respectively.

Identified metabolites in the tested crop parts accounted for 90–94% of the TRR in forage, 84% of the TRR in straw and 94% of the TRR in grain.

The prothioconazole-desthio was slowly metabolized in wheat. It was the dominant constituent of the residue in forage (77% of TRR) and straw (72% of TRR) at harvest. However, it was only detected in small amounts in grain (0.07 mg/kg), where the residue was mainly made up by triazolylacetic acid (0.91 mg/kg) and triazolylalanine (1.72 mg/kg). Free 1,2,4-triazole was not detected in any of the crop parts.

The behaviour and metabolism of phenyl- and triazole-labelled prothioconazole were investigated after 3 spray applications with EC 250 formulation to peanuts at a rate of 297 g as/ha/application.

The total radioactive residue (TRR) levels in peanut hay were 107.5 mg/kg and 47.4 mg/kg (parent equivalents) for the phenyl- and triazole-labelled parent compound, respectively. The TRR in

nutmeat was 0.29 mg/kg and 1.4 mg/kg (parent equivalents) for the phenyl- and triazole-label, respectively. Identified metabolites accounted for 74% and 77% of the TRR in peanut hay and 65% and 83% of the TRR in nutmeat for the phenyl- and triazole-label, respectively.

Following the treatments with phenyl-labelled parent compound, the major metabolites in peanut hay included prothioconazole-desthio *(*28% of TRR, 30 mg/kg) and its derivatives *(M14/M15) amounting to* 7.3% of TRR, 7.8 mg/kg and 2.0% of TRR, 2.2 mg/kg, respectively. In addition to the parent compound two other metabolites of prothioconazole were identified as prothioconazole-sulfonic acid and *M03* (2.1% of TRR, 2.3 mg/kg and 1.6% of TRR, 1.7 mg/kg, respectively). None of these compounds were detected in nutmeat. Furthermore, metabolites derived from prothioconazole-desthio and *M02* but lacking the aromaticity of the phenyl ring were detected in the hay and in the case of prothioconazole-desthio derivatives in nutmeat too. But the main portion of radioactivity (48% of TRR in the MSPD extracts) of the nutmeat was characterized as natural occurring oil, and was determined as fatty acids.

When triazole labelled parent compound was applied the metabolites identified in peanut hay included prothioconazole-desthio (as main metabolite, 24% of the TRR, 11 mg/kg) and its hydroxylated derivatives (*M14, M15* amounting to 6.6% of TRR, 3.1 mg/kg and 3% of TRR, 1.4 mg/kg, respectively). Two other metabolites of prothioconazole were identified as *M02* and *M03* (2.7% of TRR, 1.3 mg/kg and 3.6% of TRR, 1.7 mg/kg, respectively). Furthermore, metabolites derived from prothioconazole-desthio and *M02* but lacking the aromaticity of the phenyl ring were detected in the hay. With the exception of prothioconazole-desthio, none of these metabolites were detected in nutmeat.

The major metabolites in nutmeat, are conjugates of 1,2,4-triazole (*M31,* 48% of TRR, 0.67 mg/kg and *M30,* 24% of the TRR, 0.34 mg/kg). However, free 1,2,4-triazole was not detected in peanuts. A small portion of the radioactivity of nutmeat (3.0% of the TRR) was characterized as fatty acids in naturally occurring oil. The detection of radiolabelled fatty acids in nutmeat is assumed to be a consequence of the mineralisation of phenyl-labelled prothioconazole to $^{14}CO_2$ in the soil which is subsequently taken up by the plant and incorporated into natural products.

Four foliar spray applications of prothioconazole were made to sugar beet plants at an average rate of 288 and 289 g as/ha/application for a total rate of 1152 and 1157 g ai/ha of the phenyl- or triazole-labelled parent compound, respectively.

The TRR levels in sugar beet tops were 4.3 mg/kg and 5.2 mg/kg (expressed as mg as equivalents/kg) for the phenyl- and triazole-labelled parent compound, respectively. The TRR in sugar beet roots was 0.12 mg/kg and 0.13 mg/kg for the phenyl- and triazole-label, respectively. Identified metabolites accounted for 65% and 69% of the TRR in sugar beet tops and 60% and 61% of the TRR in the roots for the phenyl- and triazole-label, respectively. Additionally, 33% and 29% of the TRR was characterized in the tops and 32% and 33% in the roots for the phenyl- and triazole-label, respectively.

When the phenyl labelled compound was used the major metabolite identified in sugar beet tops were prothioconazole-desthio *(28% of TRR, 1.2 mg/kg)* and isomers of its hydroxyl-glucosides *(M21/M22/M23)*, *M24* and *M59*. In the sugar beet roots only prothioconazole-desthio (58% of the TRR, 0.068mg/kg) and *M03* were identified. In addition to the parent compound, the following metabolites were identified in sugar beet tops: *M03*, *M24*, *M59* and *M60*. In the sugar beet roots only prothioconazole-desthio (25% of the TRR, 0.033 mg/kg) and *M03* was identified.

In the case of treatment with triazole labelled compound, the metabolites identified in sugar beet tops were prothioconazole-desthio (19% of the TRR, 0.99 mg/kg), and the corresponding hydroxy-glucoside isomers *(M21/M22/M23).*

Prothioconazole was extensively metabolized in sugar beets to numerous components; only a small quantity of unchanged prothioconazole was detected (5–7% of TRR from triazole and phenyl labelled studies). The major metabolite was prothioconazole-desthio arising from oxidation of the sulfur of the triazolinthione ring to form the corresponding sulfonic acid with subsequent elimination of the sulfonic acid group. Hydroxylation of the phenyl ring and/or benzylic carbon to form multiple

monohydroxy isomers was observed with subsequent conjugation with glucose or further reaction to produce *M24*. The triazole moiety was released leading to triazolylalanine and triazolylhydroxyl-propionic acid. These metabolites may also have been formed as a result of 1,2,4-triazole uptake from the soil followed by immediate conjugation. Free 1,2,4-triazole was not detected suggesting an immediate conjugation of the released triazole. Additional triazole-label specific metabolites were formed by elimination of the chlorophenyl moiety *(M45, M46* and *M62).* The metabolic pathway is similar to that seen in peanuts and spring wheat conducted with phenyl- or triazole-labelled prothioconazole.

In summary, irrespective of the crop or application mode (foliar or soil), the major metabolites found in all crops were prothioconazole-desthio and, specific to the triazole-label studies, the metabolites triazolylalanine, triazolylhydroxypropionic acid and triazolylacetic acid. Based on the results of these studies it was postulated that 1,2,4-triazole *(M13)* was taken up from the soil and transformed directly in the plants to these metabolites. No free 1,2,4-triazole was detected in any matrix, either in the target plant metabolism studies or in the confined rotational crops study.

Environmental fate

Prothioconazole is a very weak acid and its water solubility is low at pH 4 and increases with increasing pH. It is readily soluble at pH 9. Its log K_{ow} increases from 2.0 at pH 9 to 4.2 at pH 4. Its vapour pressure and volatility are low.

Prothioconazole was found to be stable at pH 7 and 9 while only very low degradation was observed at pH 4. Hydrolysis is of minor importance for its degradation in the environment.

The photodegradation of prothioconazole was studied in sterile aqueous buffer solution at pH 7 and 25 °C using [phenyl-UL-^{14}C] and [3,5-Triazole-^{14}C]prothioconazole. Under the experimental conditions prothioconazole was completely photodegraded. Experimental half-lives were determined to be 48 h (mean of two labels). Prothioconazole-desthio was identified as main degradation product at a maximum level of 56% of the applied radioactivity. Two further major metabolites were identified as prothioconazole-thiazocine at 15% and 1,2,4-triazole at 12%. Recovery at the latest sampling intervals ranged from 104% to 107% of the applied radioactivity.

The experimental data indicate that the solar radiation contributes to the primary degradation and elimination of prothioconazole in aquatic systems of the environment.

Aerobic degradation of prothioconazole was studied in several soils under laboratory conditions in the dark applying the test substance at about 600 g ai/ha treatment, equivalent to the maximum recommended field application rate for one growing season.

The amount of radioactivity, expressed in percent of applied radioactivity, bound to soil increased during the test period and reached a maximum and then decreased until the end of the test period. In the course of the studies, the amounts of radioactivity which could be extracted decreased. At all sampling intervals, no volatile organic compounds were found (< 0.1% of the applied radioactivity). Prothioconazole was rapidly degraded in soil under aerobic conditions to CO_2, the final degradation product. Parallel to mineralisation, bound residues were formed. The calculated DT_{50} values of prothioconazole determined in the laboratory soil degradation studies were in the range of 0.07 to 1.3 days. The DT_{50} values of the two major metabolites prothioconazole-S-methyl and prothioconazole-desthio determined in the laboratory trials were in the range of 5.9 to 46 days and 7.0 to 34 days, respectively.

A total of eight metabolites were identified or characterized in the soil extracts along with the parent compound and $^{14}CO_2$. The major metabolites (> 10% of the applied radioactivity) were *M01* and prothioconazole-desthio, which were both degradable under aerobic conditions and thoroughly metabolized to carbon dioxide. Prothioconazole -sulfonic acid, *M03*, *M13*, *M14, M15, M16*, *M17* and *M20* were found as minor metabolites.

Eight field trials were conducted at different sites in northern and southern Europe. The DT_{50} values for prothioconazole ranged from 1.3 to 2.8 days (mean: 1.7 days). The corresponding DT_{90}

values were in the range of 4.4 to 9.3 days (mean: 5.8 days). The dissipation times for prothioconazole-desthio ranged from 16 to 72 days (mean: 42 days), the corresponding DT_{90} values ranged from 54 to 240 days (mean: 140 days). Prothioconazole-S-methyl concentrations never exceeded the LOQ of 6 µg/kg, corresponding to less than 3% of the initial concentration of the active substance. No residues of prothioconazole or its metabolites were detected at a depth below 10 cm in the soil, with the exception of the day 89 in one trial, where residues of prothioconazole-desthio were detected between the LOD and the LOQ in the 10–20 cm layer.

Crop rotation studies

Two confined rotational crop studies were conducted in wheat, Swiss chard and turnips using phenyl- and triazole-labelled parent compound. The phenyl-labelled prothioconazole was applied once at a rate of 578 g as/ha, while four applications were made to the soil with the triazole-labelled prothioconazole at an average rate of 204 g as/ha/application. The triazole labelled compound gave higher residue concentrations ranging from 0.25 to 0.57 mg/kg in wheat forage, from 2.0 to 2.6 mg/kg in wheat hay, 1.4 to 1.7 mg/kg in wheat straw and from 3.8 to 5.9 mg/kg in wheat grain. The highest residues were observed either in the 2nd or 3rd rotations except wheat straw showing the highest residue in 1st rotation.

In the study using the triazole-labelled prothioconazole the major metabolites found in all matrices were triazolylalanine, triazolylhydroxypropionic acid and triazolylacetic acid. No free 1,2,4-triazole was detected in any matrix. Minor metabolites detected in most matrices were prothioconazole-desthio *(*except wheat grain*))*, *M18*, *M45*, and *M46*. The concentrations of minor metabolites common to both labels were lower than both identification triggers (<< 10% of TRR and < 0.05 mg/kg).

The parent compound was present if detected at all at < 0.005 mg/kg, prothioconazole-desthio was detected in all parts of the wheat plants and amounted to 0.045 mg/kg in wheat straw in the 1st rotation. Conjugation played an important role in the degradation of prothioconazole.

Field rotational crop trials were conducted at three locations in the USA (Georgia, Indiana and Kansas) to measure the magnitude of prothioconazole residues in field crops at 1-, 4-, 8-, and 12-month plant-back intervals (PBIs) following the use of the 480 SC formulation on a target crop.

Each trial contained a control and a treated plot. Two foliar spray applications with the 480 SC were made 14 (±2) days apart to bare soil in the treated plot. The total application rate was about double (800 g/ha) that of the highest label rate for prothioconazole in USA. The total prothioconazole derived residue was less than the LOQ of 0.05 mg/kg (0.02 mg/kg for grain only) in all crop RACs at the 1-month PBI. No further analyses were conducted.

It can therefore be stated that no residues above respective LOQs of 0.02 and 0.05 mg/kg would be expected in rotational crops, for human consumption, following the use of prothioconazole at maximum application rates.

Methods of analysis

The meeting received a number of validated analytical methods for the determination of residues in plant, animal tissue, milk and soils.

The residue components detected and the basic principles of the methods are summarized below.

Prothioconazole-desthio was determined with the extended DFG method S 19 in combination with GPC cleanup and GC/MS detection. The LOQs were for plant commodities were 0.02 mg/kg (tomato, orange, wheat grain, and rape seed), 0.05 mg/kg (wheat forage and straw), and for commodities of animal origin 0.01 mg/kg (milk) and 0.02 mg/kg (meat, egg and fat).

Parent prothioconazole, prothioconazole-desthio and prothioconazole sulfonic acid were extracted from plant materials with a mixture of methanol (MeOH), 30% hydrogen peroxide (H_2O_2), and aqueous sodium bicarbonate ($NaHCO_3$) at 65 °C. This extraction procedure converts

prothioconazole to a mixture of prothioconazole-sulfonic acid and prothioconazole-desthio. The unchanged prothioconazole-desthio residues are extracted directly. After cleaning the extracts the residues were determined with HPLC/MS/MS. The method was validated in barley hay, straw, and grain, canola grain, mustard greens, peanut hay and nutmeat, rice straw and grain, turnip tops and roots, wheat forage, hay, straw, and grain, and wheat bran, flour, germ, middlings and shorts. The LOQ ranged between 0.02 and 0.05 mg/kg depending on the sample matrix. The method requires specific instrument setup, and stabile isotopes as internal standards consequently it is not readily applicable for enforcement purposes.

Other methods are also available for the prothioconazole sulfonic acid and prothioconazole-desthio, or prothioconazole and prothioconazole-desthio in various pant matrices with LOQs ranging from 0.01 to 0.05 mg/kg depending on the sample material.

Residues of prothioconazole-desthio, prothioconazole-3-hydroxy-desthio and prothioconazole-4-hydroxy-desthio, and conjugates that can be converted to one of these compounds via acid hydrolysis in matrices of animal origin can be determined by HPLC-MS/MS (Method 00655 plus modifications). Homogenized sample materials of meat, liver and kidney were extracted twice with a mixture of acetonitrile/water, and centrifuged, each. The supernatant was evaporated to the aqueous remainder, then diluted with water, acidified and refluxed for 2 h. Milk samples were hydrolysed and purified directly after dilution with water. This hydrolysis step was performed to convert non-aromatic precursor compounds and glucuronic acid bound analogues into prothioconazole-desthio-3-hydroxy and prothioconazole-desthio-4-hydroxy. Quantification was carried out with HPLC-MS/MS. The LOQ for milk was 0.004 mg/kg and for meat, liver, kidney and fat 0.01 mg/kg.

Comparison of chromatographic profiles before and after hydrolysis clearly shows that groups of minor unidentified metabolites have disappeared. In their place the compounds with a common moiety, i.e., prothioconazole-desthio, *M14*, *M15*, *M33* and *M35* are emerging or increasing. Since the major part of the radioactivity (58–84%) is recovered, and the proportion of identified/characterized residues is higher after acid hydrolysis than without hydrolysis in milk, kidney and muscle and similar in liver and fat, it can be concluded that a significant proportion of the unidentified compounds are converted to the common moiety products.

Prothioconazole, prothioconazole-desthio, and prothioconazole-4-hydroxy residues in various bovine matrices can also be determined by LC-MS/MS (Method JA006-A04-02). This method is based on extraction with acetonitrile/water containing 250 mg/mL L-cysteine HCl (4:1 v/v), and hydrolysis of the extracts with 5N HCl under reflux for 2 hours. Prothioconazole, prothioconazole-desthio prothioconazole-4-hydroxy are quantified individually. The LOQ for each of the three analytes are: 0.004 mg/kg for milk; 0.010 mg/kg for skim milk, cream, and muscle; 0.010 mg/kg for liver; 0.010 mg/kg for kidney; and 0.050 mg/kg for fat.

Stability of pesticide residues in stored analytical samples

Freezer storage stability of metabolite prothioconazole-desthio, the main residue component in plants was examined in wheat, canola (seed, pod, straw), spinach (leaves), sugar beet (root, leaf with root collar), tomato (fruit), and field pea (field pea dried) at about minus 18 °C or below. The results demonstrate that, under freezer conditions, residues of prothioconazole-desthio were stable over a storage period of up to 36 months in wheat and at least 24 months for the other crops.

The storage stability periods are longer than the longest period of time for which samples from European field residue trials presented in this dossier were stored prior to analysis (cereals and oil seed rape).

The prothioconazole and prothioconazole-desthio residues were found to be stable (< 30% decomposition) in wheat hay, wheat straw, canola seeds, mustard greens, turnip root and tomato fruit during 36–42 months of freezer storage.

Residue definition

Prothioconazole is extensively metabolized and the most important pathways for metabolism are common to wheat, peanut and sugar beet. The nature of the residue found in wheat after foliar spray application, seed treatment and as a rotational crop was similar.

The majority of the metabolites are simply multiple structural isomers of monohydroxylated prothioconazole-desthio *(M14-M17)* and their conjugates [glucosides *(M21-M23)* and malonyl-glucosides*(M54-M56)*], and prothioconazole-dihydroxy-olefin and its conjugates. Oxidative hydroxylation led to isomers of prothioconazole-dihydroxy-diene and their conjugates. Although the sum of these compounds and their conjugates were as high as 42% of the TRR in an individual crop matrix, these conjugated and/or hydroxylated metabolites represented individually < 10% of the TRR in the plant matrices.

The proportion of parent prothioconazole was low in wheat grain, wheat forage, wheat hay, straw, peanut hay, peanut nutmeat , sugar beet tops, sugar beet roots, sugar beet forage and in rotational crops if detected at all.

Irrespective of the crop or application mode, the major metabolites found in all crops were prothioconazole-desthio and triazolylalanine, triazolyl-hydroxy-propionic acid and triazolylacetic acid. The major plant metabolite, prothioconazole-desthio was slowly metabolized in wheat. It was the dominating constituent of the residue in forage and straw at harvest. However, it was only detected in small amounts in grain where the residue was mainly made up by triazolylacetic acid and triazolylalanine. No free 1,2,4-triazole was detected in any matrix either in the target plant metabolism studies or in the confined rotational crops study.

The metabolic profiles for milk and the edible tissues and organs showed that parent prothioconazole was a major compound in all tissues and organs but only of minor importance in milk. Compounds detected in all matrices in the study with phenyl-labelled prothioconazole-desthio were prothioconazole-desthio (except for milk), *M32*, *M74, M52*, and sulfate conjugates of prothioconazole-desthio-hydroxy, prothioconazole-desthio-dihydroxy, prothioconazole-desthio-hydroxy-methoxy in laying hens.

Following the administration of triazole labelled prothioconazole the only label specific metabolite identified was thiocyanate. Triazole derivatives or free 1,2,4-triazole were not found at concentrations above 0.01 mg/kg in any goat matrix. Free triazole did not exceed a residue level of 0.04 mg/kg in laying hen matrices.

The most abundant metabolite was prothioconazole-S-glucuronide. Prothioconazole-desthio was also present in all sample materials, but in much lower concentrations than prothioconazole-S-glucuronide. An exception was fat in hen and goat and eggs in hen, in which prothioconazole-desthio was predominant. In eggs and all edible tissues of hen metabolite prothioconazole-S-methyl was additionally identified. Animal feeding studies showed that the residues are not concentrated in fat of meat or milk cream. As the total residue composed of several hydroxy derivatives and their conjugates, the Meeting concluded that the residues of prothioconazole are not fat soluble.

There are analytical procedures for the determination of prothioconazole residues in various combinations. A GC/MS multi residue method has been validated for the determination of prothioconazole-desthio. An LC-MS/MS total residue method converts prothioconazole, its metabolites and their conjugates to a mixture of prothioconazole sulfonic acid and prothioconazole-desthio. Another method is suitable for the determination of prothioconazole-desthio, prothioconazole-3-hydroxy-desthio and prothioconazole-4-hydroxy-desthio and conjugates that can be converted to one of these compounds via acid hydrolysis in/on matrices of animal origin by HPLC-MS/MS. The major part of the TRR (58–84%) is recovered with this method.

Supervised trials indicated that residues measured as the sum of prothioconazole sulfonic acid and prothioconazole-desthio were higher than the prothioconazole-desthio alone.

The Meeting noted that 1,2,4-triazole, triazolyl-acetic acid and triazolyl-alanine may be derived from several sources. Field trials performed in USA indicated that the sum of the conjugates

of triazolyl-alanine and triazolyl-acetic acid amounted to a maximum of 0.92 mg/kg and 1.76 mg/kg in barley and wheat grain, 0.66 mg/kg in canola seed and 3.39 in peanut meat. However, free 1,2,4 triazole was not detected in any of the samples above the LOQ. These findings agree with the information obtained from metabolism studies. As these compounds may be present in food commodities from different sources they are not suitable for enforcement purposes. The relatively low level of conjugated residues in food commodities and the low toxicity of triazolyl-acetic acid and triazolyl-alanine (max ADI of 1 mg/kg) do not justify their inclusion for dietary risk assessment.

Taking into consideration the toxicological significance of the metabolites, the major residues in plant (including the fact that animal feed commodities are almost free of the parent prothioconazole) and animal commodities and the practicality of enforcing the residue limits, the Meeting recommends the following residue definition: for both enforcement and dietary risk assessment:

for plant commodities for enforcement and dietary risk assessment: *prothioconazole-desthio*,

for animal commodities for enforcement: prothioconazole-desthio; and for dietary risk assessment: *the sum of prothioconazole-desthio, prothioconazole-desthio-3-hydroxy, prothioconazole-desthio-4-hydroxy and their conjugates expressed as prothioconazole-desthio*.

Results of supervised residue trials on crops

The meeting received supervised trial data for prothioconazole uses on barley, wheat, triticale (one seed dressing trial), dried beans and peas, oil seed rape and canola, sugar beet, soya bean and peanut. Prothioconazole was applied as a foliar spray using an EC (emulsifiable concentrate), SC (suspension concentrate) formulation, and for seed dressing of cereals using a FS (flowable concentrate) formulation. The both use patterns are permit for use on cereals.

The trials were performed in Brazil, Canada, Europe and USA. Labels and English translations, where necessary, were provided from 20 countries.

The trials were performed in compliance with GLP and good documentation was provided.

In the Brazilian and European trials the main plant metabolite prothioconazole-desthio was determined. In the Canadian and US trials the residues of parent prothioconazole and its metabolites were converted to a mixture of prothioconazole-desthio and prothioconazole-sulfonic acid (both expressed as parent molar equivalents) and summed with unchanged prothioconazole-desthio (expressed as parent molar equivalents) to give a total prothioconazole derived residue. The methods applied were validated by recovery experiments prior to and concurrent with the residue analyses. The performance of the methods concurred with the current quality requirements.

In trials from Brazil, Canada and USA only the total residue was reported, though the individual residue components were measured separately. Thus the presentation of the results did not comply with the *FAO Manual* specifying that individual residue data should be reported separately (Analysis of samples, page 25) and could not be used for estimation of residue levels.

Pulses (dried beans and peas)

Supervised trials on dried peas (13) and dried beans (10) were carried out with 3 foliar applications of a SC 480 formulation at a target rate of 200 g/ha/application in Canada (9) and USA (14) corresponding to US GAP.

Only total residues were reported.

Sugar beet

The Meeting received reports of 12 residue trials on sugar beets from the USA complying with the US GAP.

Only total residues were reported.

Cereal grains

A total of 123 trials were carried out on cereals (wheat, triticale and barley) with the SC 480, EC250 and FS200 formulations in Canada, Europe and the USA. Only total residues were reported from the USA and Canadian trials.

In Germany, Ireland, and the UK one seed dressing and up to 3 foliar applications for wheat and rye, and a maximum of 2 applications for barley and oat can be made at a rate of 200 g ai/ha. The PHI is 35 days in Germany, and the last treatment should be made at growing stage of BBCH 69–71 in the UK.

The maximum registered application rates for barley, oat, triticale and wheat seed treatments are 100 mg ai/kg of seed in the UK, 75 mg/kg in France and 25–50 mg/kg in Germany. The registered rates in other European countries are within this range or lower in few cases.

A total of 17 trials on barley were reported from Germany, France, Italy, Spain ,Sweden and the UK, where three applications were made at each site: one seed dressing with a nominal rate of 150 mg ai/kg seed and two foliar applications with 200 g ai/ha. The seed dressing rate was 1.5 times higher than the recommended label rate.

The prothioconazole-desthio residues in barley grain at 35–57 days, matching the PHI or growing stage specified on the label, were: < 0.01 (10), 0.01, 0.01, 0.02 (4) mg/kg.

In 19 European trials on wheat, the application rate for seed dressing was approximately double the GAP rate and 3 foliar applications were made instead of two in South European trials. Nevertheless, no prothioconazole-desthio residue could be detected (< 0.01 mg/kg) in any of the 16 grain samples taken at 35 days post application, or 16 samples taken between 42–64 days after last application, except in one trial conducted in the UK where 0.32 mg/kg residue was found.

Taking into account the total residues derived from similar application rates (0.6 mg/kg in barley and 0.061 mg/kg in wheat) the Meeting concluded that the 0.32 mg/kg residue value was atypical and was not considered.

Based on the similar residue data on barley and wheat available from European trials and the similar use patterns for cereals, the Meeting estimated an STMR value of 0.01 mg/kg and a maximum residue level of 0.05 mg/kg for barley, oat, rye, triticale and wheat.

Oils seeds

A total of 34 trials on rape/canola were carried out with either an EC250 or SC 480 formulations. The trials were performed in Canada (16), France (7), Germany (2), the UK (2), Sweden (1) and the USA (6).

In the 22 Canadian and USA trials only the total residue was reported.

In France, Germany, the UK and several other countries in Europe the application rate is within 125–175 g/ha and the PHI ranges between 35 and 56 days.

The European trials were performed with 2 applications at 175 g ai/ha nominal rate and samples were collected 56 to 67 days after the second treatment, which correspond to the GAP of the UK.

The prothioconazole-desthio residues derived from trials evaluated against the UK GAP were: < 0.01 (7), 0.01 (3) and 0.02 mg/kg.

The Meeting estimated a maximum residue level of 0.05 mg/kg and STMR of 0.01 mg/kg for rape seed.

Peanut

The GAP in the USA permits 4 applications at a rate of 200 g ai/ha (800 g ai/ha/season) at 14 days intervals and 14-day PHI. The hay and by-products cannot be fed to animals.

In 12 trials from the USA, performed according to GAP, the total residues in nutmeat were below the LOQ (< 0.02 mg/kg) in all samples.

The Meeting noted that the metabolism studies indicated very low residues in nutmeat and no total residue was detected in any of the samples, and decided to use the total residue data for estimating a maximum residue level of 0.02* mg/kg and an STMR of 0.01 mg/kg.

Soya bean

The GAP of the USA specifies 3 applications at a maximum rate of 105 g/ha and 21 days PHI. No information was available on permitted Brazilian uses. Nineteen US trials did not comply with GAP, and only the total residue was reported.

Primary feed commodities

The basic information on registered uses is provided under food commodities. Only the relevant residue data are summarized below.

Total residues in soya bean forage and hay and sugar beet tops derived from supervised trials were recorded, but not evaluated by the Meeting. The total residues in peanut hay were not considered as it is not allowed to be used as an animal feed in the USA where the trials were conducted.

Cereal forage and straw

The Meeting noted that forage samples were taken up to 28 days after last application. However, several countries labels do not contain any restriction on grazing. As the 7-day sampling interval was considered the shortest under practical conditions, residues measured at 7 days were used for estimation of animal dietary burdens.

In North European trials the prothioconazole-desthio residues in wheat forage at 7 days post-application were: 0.11, 0.32, 0.57, 0.65, 0.78, 0.89, 0.92, 1.0, 1.1, and 1.8 mg/kg.

In barley forage at the 7 day sampling the residues were: 0.6, 0.85, 1.0, 1.2, 1.7(2), 2.0 and 2.6 mg/kg.

The Meeting noted that the residues in barley and wheat forage were in the same range, and based on the combined data (0.11, 0.32, 0.57, 0.60, 0.65, 0.78, 0.85, 0.89, 0.92, 1.0, 1.0, 1.1, 1.2, 1.7, 1.7, 1.8, 2 and 2.6 mg/kg) estimated a STMR of 0.96 mg/kg and a highest residue of 2.6 mg/kg for barley, oat, rye, triticale and wheat forage.

In wheat straw (between 35 and 64 days after last treatment) the residues were: 0.08, 0.09, 0.11, 0.14, 0.15, 0.19, 0.20, 0.25, 0.27, 0.31, 0.42, 0.47, 0.52, 0.53, 0.72 (3), 0.77 and 1.0, mg/kg.

In barley straw (between 35–57 days) the residues were: 0.08, 0.1, 0.1, 0.13, 0.13, 0.14, 0.14, 0.16, 0.19, 0.24, 0.3, 0.38, 0.53, 0.75, 1.1, 1.1 and 1.2 mg/kg.

The Meeting considered the barley and wheat straw residue data were from the same population and based on the combined residue data (0.08, 0.08, 0.09, 0.1, 0.1, 0.11, 0.13, 0.13, 0.14, 0.14, 0.14, 0.15, 0.16, 0.19, 0.19, 0.20, 0.24, 0.25, 0.27, 0.3, 0.31, 0.38, 0.42, 0.47, 0.52, 0.53, 0.53, 0.72(3), 0.75, 0.77, 1.0, 1.1, 1.1, and 1.2 mg/kg) estimated on dry weight basis a STMR of 0.30 mg/kg (median value of 0.26 uncorrected for moisture content) and highest residue of 1.36 and a maximum residue level of 2 mg/kg, for barley, oat, ray, triticale and wheat straw.

Rape forage

Samples of green forage were only taken at day 0. The residues present in day 0 samples do not represent the practical situation and cannot be used for estimation of animal burden.

Fate of residues during processing

A hydrolysis study with [Phenyl-UL-^{14}C]prothioconazole in buffered drinking water was conducted under conditions representative for core processing procedures in order to determine their possible

influence on the nature of the residues. The samples were incubated at 90 °C at pH 4 for 20 minutes (pasteurisation), l00 °C at pH 5 for 60 minutes (baking, brewing and boiling) and l20 °C at pH 6 for 20 minutes (sterilisation).

HPLC analyses of incubated samples demonstrated that prothioconazole degraded slightly (≤ 11%) to prothioconazole-desthio at l20 °C at pH 6.

A field trial was conducted to measure the magnitude of prothioconazole residues in/on wheat grain, aspirated grain fractions, bran, flour, germ, middling, and shorts following two foliar spray applications of prothioconazole 480 SC to wheat at five-fold exaggeration of the maximum recommended label use rate.

Mature wheat grain was harvested 47 days after the last treatment, and processed with a procedure which simulated commercial processing practices.

The residues of prothioconazole and prothioconazole-desthio were measured as prothioconazole-desthio and prothioconazole sulfonic acid. The individual residues were summed to give a total prothioconazole derived residue. The LOQ for total residue was 0.02 mg/kg for wheat grain, bran, flour, germ, middling, and shorts, and 0.25 mg/kg for aspirated grain fractions.

The total residues of prothioconazole in grain at harvest were 0.05 mg/kg. The corresponding residues in aspirated grain fraction were 12.5 mg/kg.

The residues in the processed products were up to 0.12 mg/kg in bran, < 0.02 mg/kg in flour, 0.10 mg/kg in germs, 0.03 mg/kg in middling and 0.05 mg/kg in shorts. No control interferences were detected. The calculated processing factors were 250 for aspirated grain fraction, 2.4 for wheat bran, 0.4 for flour, 2 for germ, 0.6 for middling and 1 for shorts.

A field trial was conducted to measure the magnitude of prothioconazole residues in canola seed, canola meal and canola refined oil following two foliar spray applications with 480 SC at 1.0 kg ai/ha, which corresponded to a five-fold (5×) exaggeration of the maximum recommended label use rate. Mature canola plants were cut 47 days after the second treatment, dried on the field for 5 days, then processed using procedures which simulated commercial processing practices.

The residues of prothioconazole and prothioconazole-desthio were measured as prothioconazole-desthio and prothioconazole sulfonic acid. The LOQ for total prothioconazole residue was 0.02 mg/kg for canola seed, meal and refined oil. The results indicated that no concentration (< 0.7×) of the total prothioconazole derived residue was seen in canola meal and refined oil.

Field trials were conducted to measure the magnitude of prothioconazole residues in peanut nutmeats, peanut meal, peanut refined oil, dry roasted peanuts and peanut butter as well as in soya bean processed commodities of meal, hulls and refined oil. The total amount of prothioconazole 480 SC applied represented a five-fold (5×) exaggeration of the maximum recommended label use rate. The processed fractions were analysed for total residues. The total prothioconazole derived residue did not concentrate (<1×) either in the peanut refined oil, dry roasted peanuts and peanut butter, or in soya bean meal and refined oil.

Farm animal feeding studies

The cattle feeding studies were conducted administering prothioconazole-desthio or the parent compound via capsules to lactating dairy cows at three dose levels for 28 or 29 consecutive days. At the end of the dosing period, the cows were sacrificed within 24 h after the last capsule treatment. The liver, kidney, fat (composite omental and perirenal), and muscle (composite of loin, elbow and flank) were collected for analysis.

Milk was collected for analysis twice daily at regular intervals during the dosing period and composited for each cow. In addition, a portion of the morning milk from one cow of the highest dose level was subjected to an accumulation test in milk fat on the day before sacrifice.

Following the administration of prothioconazole-desthio at rates of 4 mg/kg feed, 25 mg/kg feed, or 100 mg/kg feed the samples were analysed for prothioconazole-3-hydroxy-desthio, prothioconazole-4-hydroxy-desthio , and prothioconazole-desthio. The LOQ were 0.01 mg/kg for muscle, liver, kidney and fat, and 0.004 mg/kg for milk.

Prothioconazole-desthio total residues, expressed as mg/kg prothioconazole-desthio equivalents, were observed in liver and kidney at all feeding levels with a linear dose relationship.

- In liver total residues ranged from 0.02 to 0.05 mg/kg at the 4 mg/kg feeding level, from 0.18 to 0.26 mg/kg at the 25 mg/kg feeding level, and from 0.61 to 1.6 mg/kg at the 100 mg/kg feeding level.
- In kidney total residues ranged from 0.01 to 0.04 mg/kg at the 4 mg/kg feeding level, from 0.11 to 0.17 mg/kg at the 25 mg/kg feeding level, and from 0.41 to 1.1 mg/kg at the 100 mg/kg feeding level. In muscle and fat, total residues were considerably lower.
- In muscle, total residues were below the LOQ (0.01 mg/kg) at the 4 mg/kg and 25 mg/kg feeding levels, and ranged from 0.01 to 0.03 mg/kg at the 100 mg/kg feeding level.
- In fat, total residues were below the LOQ (0.01 mg/kg) at the 4 mg/kg feeding level, and ranged from 0.01 to 0.02 mg/kg at the 25 mg/kg feeding level, and from 0.03 to 0.14 mg/kg at the 100 mg/kg feeding level.
- from a single population or the equivalent of a single population;

Prothioconazole-desthio total residues in milk at the highest dose level increased from < 0.004 mg/kg (day 1) to a plateau level (day 4 to day 29) of 0.006 to 0.010 mg/kg for two animals and of 0.013 to 0.021 mg/kg for one animal, while no residue could be detected at lower dose levels. Liquid-liquid-partitioning of whole milk against n-hexane showed that prothioconazole-desthio was in milk fat and the 3-hydroxy and 4-hydroxy metabolites (M14 and M15) remained in the aqueous phase. However, the total residues remained preferentially in the aqueous phase, i.e., 0.015 mg/kg with only 0.004 mg/kg in the n-hexane phase, indicating no accumulation in milk fat.

When cows were dosed with the parent compound at levels of 9.9 mg/kg feed, 29.5 mg/kg feed, and 98.4 mg/kg feed, the samples were analysed for prothioconazole, prothioconazole-desthio and prothioconazole-4-hydroxy. The LOQ for the total residue was 0.005 mg/kg in milk; 0.01 mg/kg in skim milk, milk cream, liver, kidney, and muscle; and 0.05 mg/kg in fat.

The total average prothioconazole-desthio residues (prothioconazole, prothioconazole-desthio and prothioconazole-4-hydroxy) at the dose groups of 9.9 mg/kg feed, 29.5 mg/kg feed, and 98.4 mg/kg feed were respectively: < 0.05 mg/kg in fat, 0.07, 0.21, and 0.80 mg/kg in kidney, 0.10, 0.28 and 0.8 mg/kg in liver, and < 0.01, 0.01 mg/kg in muscle.

The highest total prothioconazole residue in the milk from the highest (5×) dose group was equal to or less than 0.006 mg/kg. All milk samples from the 29.5 mg/kg (1.5×) dose group contained < 0.005 mg/kg (< LOQ) total prothioconazole residue. Minimal concentration (1.1× concentration) of prothioconazole residues occurred in cream and no concentration (<1× concentration) occurred in skim milk.

Poultry

A summary of a feeding study with laying hens was provided. In this study three groups of laying hens were dosed via capsule for 29 consecutive days with 0.26, 0.79, and 2.6 mg/kg feed/day. Following the administration of the highest dose, the total prothioconazole residues (sum of prothioconazole-desthio, prothioconazole-4-hydroxy and prothioconazole) were below the LOQ in eggs (< 0.005 mg/kg) and liver, muscle and fat (< 0.01 mg/kg) samples.

Farm animal dietary burden

The Meeting noted that the feeding study conducted with parent prothioconazole does not represent the practical residue situations where the feed items contained only low levels (< 5%) of the parent compound while the major part of the residue was the prothioconazole-desthio. Consequently, the dietary burden was calculated from the prothioconazole-desthio residues measured in feed commodities and it was compared to the residues found in animal commodities after the administration of prothioconazole-desthio.

The Meeting estimated the dietary burden in farm animals on the basis of the diets listed in Annex 6 of the 2006 JMPR Report (OECD Feedstuffs Derived from Field Crops). Calculation from highest residue, STMR for some bulk commodities and STMR-P values provides the levels in feed suitable for estimating MRLs, while calculation from STMR and STMR-P values for feed is suitable for estimating STMR values for animal commodities.

Estimated maximum and mean dietary burdens of farm animals

Dietary burden calculations for beef cattle, dairy cattle are provided in Annex 6 of the 2008 Report of the JMPR.

		Animal dietary burden, total prothioconazole ppm of dry matter diet		
		US-Canada	EU	Australia
Beef cattle	max	2.61	2.61	**10.40**[a]
	mean	0.96	0.96	**3.84**[b]
Dairy cattle	max	4.17	2.60	**7.80**[c]
	mean	1.55	0.96	2.75

[a] Highest maximum beef or dairy cattle dietary burden suitable for MRL estimates for mammalian meat.

[b] Highest mean beef or dairy cattle dietary burden suitable for STMR estimates for mammalian meat.

[c] Highest dairy cattle dietary burden suitable for STMR estimates for mammalian milk.

Dietary burden calculations for poultry

		Animal dietary burden, total prothioconazole ppm of dry matter diet		
		US-Canada	EU	Australia
Broiler chicken	max	0.009	0.008	0.008
	mean	0.009	0.008	0.008
Laying	max	0.009	1.050[a]	0.006
	mean	0.009	0.39[b]	0.006

[a] Highest maximum dietary burden suitable for MRL estimates for poultry meat and eggs.

[b] Highest mean dietary burden suitable for STMR estimates for poultry meat and eggs.

Animal commodity maximum residue levels

Based on the linear relationship observed for the maximum residues in various tissues of cattle and the results of the metabolism studies, the expected maximum prothioconazole-desthio residue derived from feeding 10.4 mg/kg feed were: 0.095 mg/kg in liver, 0.065 mg/kg in kidney, 0.009 mg/kg in meat, and 0.01 mg/kg in fat.

In milk the highest dose resulted in a maximum of 0.02 mg/kg residue, and no residue (< 0.004 mg/kg) could be detected at lower dose levels. Consequently, no residue is expected in milk where the feed contains residues up to 7.8 mg/kg.

The STMR residues estimated from the 3.84 mg/kg median residue intake are: < 0.01 in liver and kidney, meat and fat.

The Meeting estimated maximum residue levels of 0.2 mg/kg for edible offal, 0.01 mg/kg in meat and fat and 0.004* mg/kg in milk. The STMR and HR values are 0.01 mg/kg for meat, 0.004 mg/kg for milk and edible offal the values are 0.05 and 0.1 respectively.

A metabolism study was carried out on laying hens with the parent prothioconazole at an exaggerated rate of 171 mg/kg feed indicated a total residue of 4 mg/kg in liver. Assuming a proportional residue level the 1.05 mg/kg residue in feed would result in 0.025 mg/kg residue in the liver.

A feeding study performed with parent prothioconazole at maximum rate of 2.59 mg/kg feed showed that the total residue would be below the LOQ in eggs (0.005 mg/kg), liver, meat and fat (0.01 mg/kg). The Meeting also noted that the study designs do not reflect the residue composition in feed and the results cannot be used for estimation of maximum residue levels or STMR values.

RECOMMENDATIONS

On the basis of the data from supervised trials and farm animal feeding studies reported by the 2006 JMPR, the Meeting concluded that the residue levels listed below are appropriate for establishing maximum residue limits and for IEDI assessment.

Definition of the residue for both enforcement and dietary risk assessment:

for plant commodities for enforcement and dietary risk assessment: prothioconazole-desthio,

for animal commodities for enforcement: prothioconazole-desthio, and for dietary risk assessment:

the sum of prothioconazole-desthio, prothioconazole-desthio-3-hydroxy, prothioconazole-desthio-4-hydroxy and their conjugates expressed as prothioconazole-desthio..

Commodity		MRL (mg/kg)		STMR (mg/kg)	HR (mg/kg)
CCN	Name	New	Previous		
GC 0640	Barley	0.05	-	0.01	
OS 0640	Barley straw	2	-	0.30	
MO 0032	Edible offal (Mammalian)	0.2	-	0.05	0.1
MM 0095	Meat (from mammals other than marine mammals)	0.01	-	0.01	0.01
MF 0100	Mammalian fats (except milk fats)	0.01	-	0.01	0.01
ML 0106	Milks	0.004*	-	0.004	
GC 0647	Oats	0.05	-	0.01	
OS 0647	Oat straw	2	-	0.30	
SO 0697	Peanut	0.02*	-	0.01	
SO 4703	Rape seed	0.05	-	0.01	
GC 0650	Rye	0.05	-	0.01	
OS 0650	Rye straw	2	-	0.30	
GC 0653	Triticale	0.05	-	0.01	
OS 0653	Triticale straw	2	-	0.30	
GC 0654	Wheat	0.05	-	0.01	
CF 1211	Wheat flour	0.05	-	0.004	
CM 0081	Wheat bran			0.024	
CF 1210	Wheat germ			0.02	
OS 0654	Wheat straw	2	-	0.30	

DIETARY RISK ASSESSMENT

Long-term intake

The International Estimated Daily Intake (IEDI) for prothioconazole-desthio was calculated from the recommendations for STMR-s for raw agricultural commodities in combination with consumption data for corresponding food commodities. The results are shown in Annex 3 of the 2008 Report of the JMPR.

The IEDI of the 13 GEMS/Food cluster diets were in the range of 0–1% of the maximum ADI of 0.01 mg/kg bw. The Meeting concluded that the long-term intake of residues from uses of prothioconazole considered by the Meeting is unlikely to present a public health concern.

Short-term intake

The International Estimated Short-term Intake (IESTI) for prothioconazole-desthio was calculated from the recommendations for STMRs and HRs for raw agricultural commodities in combination with consumption data for corresponding food commodities. The results are shown in Annex 4 of the 2008 Report of the JMPR.

The IESTI for women of child bearing age is 0–6% of the ARfD of 0.01 mg/kg bw. The IESTI for children and general populations is 0% of the ARfD of 1 mg/kg bw.

The Meeting concluded that the short-term intake of residues from uses of prothioconazole considered by the Meeting is unlikely to present a public health concern.

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